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MANGANESE; ITS OCCURRENCE, MILLING, AND METALLURGY

PART IV.

CHAPTER 9. FERROUS ALLOYS OF MANGANESE AND THEIR USE IN THE STEEL INDUSTRY

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G. R. FITTERER AND M. B. ROYER

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UNITED STATES BUREAU OF MINES

MANGANESE: ITS OCCURRENCE, MILLING, AND METALLURGY[1]

PART IV

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CHAPTER 9. FERROUS ALLOYS OF MANGANESE AND THEIR USE IN THE STEEL INDUSTRY

By G. R. Fitterer[2] and M. B. Royer[3]

HISTORICAL REVIEW

The application of manganese in iron and steel metallurgy is very interesting historically. In general, ancient irons and steels contained virtually no manganese, probably because the available iron ores contained only small amounts of the manganese oxides. Occasionally, samples of ancient irons were found to have appreciable amounts of manganese, but their presence is considered accidental and dependent upon the ore available to craftsmen of that time. Two specimens of iron (139)[4] made in 500 A.D. contained negligible quantities of manganese. A sample of steel which constituted the base of the Khan Baba pillar in India was probably processed in 125 B. C. by the cementation of wrought iron. This material contained 0.02 percent manganese and 0.70 percent carbon (20). One Damascus-steel sword forged some time between 1160 and 1400 A. D. was found to contain 0.14 percent manganese and 0.61 percent carbon. The manganese content of this blade was much higher than that of any other material of this type which has been analyzed. In every other instance the manganese content was below 0.02 percent.

A cast steel manufactured by the East India Co. in India in the early nineteenth century, under the name of Wootz steel, contained rather appreciable amounts of manganese. This material was made by melting and refining fairly high-manganese pig iron prepared from high-manganese ore. Heath (106), who was working at the Co. plant between 1820 and 1840, was convinced that the manganese content of the steel was the determining factor in its high quality. He learned of certain difficulties English steel manufacturers were having in making even fair-grade steel, and analyses of the material indicated low manganese contents. This convinced him that if the use of manganese could be introduced in England its steel would be greatly benefited. In consequence, he moved to England and soon was producing certain grades of ferromanganese for use with the crucible process. He recommended addition of this metallic material to the ingot mold just before pouring. It was soon found that inferior brands of steel containing only traces of manganese could be greatly improved by such additions. All metallurgists of that time became convinced

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4 Throughout parts I to IV, numbers in parentheses refer to items in this bibliography, and page numbers to those in the reference cited.

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that manganese increased the weldability and malleability of iron.

Heath patented the use of ferromanganese in crucible-steel practice but later stated that the same effects could be produced by adding manganese ore and charcoal to the steel in the crucible. This procedure was found to be satisfactory and was used instead of his patented process.

Bessemer (106) then became interested, through his contacts with Heath, in the possibilities of increasing the quality of the product of his converter by means of manganese additions. Bessemer prepared ferromanganese by reducing iron and manganese oxides with charcoal in the crucible furnace. At the time of Bessemer's experiments Mushet (106) patented a triple alloy of manganese, iron, and carbon and recommended the use of this material as an addition agent in the bessemer process. This patent was ignored after several years because it was found that such material was already in use in special forms of high-manganese pig iron from Scotland and spiegeleisen (containing about 8 percent manganese) from Germany. The manganese content of these materials had not been previously considered in this connection. Bessemer continued his experiments on the preparation of ferromanganese and interested a chemist named Henderson (106) in the manufacture of a high-grade ferromanganese. Bessemer was particularly interested in obtaining an alloy containing about 75 percent manganese and 2 to 3 percent carbon, so that it could be added to the low-carbon steels made by the bessemer process without appreciably raising the carbon content. Henderson was able to make such material, and the use of the bessemer converter was greatly enhanced by the development of this alloy. The material was added to the ladle just before pouring, and analyses of steels made during this period indicated that the standard practice was to add 0.15 to 0.25 percent manganese in this manner. The beneficial effects of this addition saved as much as 40 percent of the material usually discarded (106).

The influence of manganese on the quality of the steel was first attributed to the reduction of dissolved oxides in liquid metal. Henderson, however, pointed out that the alloyed manganese might improve the physical properties of the iron and furthermore might react with the sulphur in the steel. He suggested investigation of these two effects. Publications in this connection, which appeared soon after his suggestion, indicated that his contentions were somewhat justified.

The effects of high percentages of manganese on the properties of iron were not discovered until 1882, when Hadfield published and patented the results of his investigations. Steels were made containing as much as 10 to 15 percent manganese, and the properties of these materials will be discussed in detail later. The following pages will also include a summary of information on the reactions of manganese in liquid steel and the effects of manganese on the properties of the finished material.

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MANGANESE IN LIQUID-STEEL METALLURGY

Sources of Manganese Used in Steel Making

During the manufacture of steel manganese is introduced in various ways. Nearly all present-day methods of manufacture involve the utilization of steel scrap, which contains variable amounts of manganese. In some processes, such as the arc electric furnace, where steel is usually made entirely from scrap, the manganese content of the finished material depends only upon the manganese content of the scrap charged and final additions of manganese-containing ferro-alloys, such as spiegel, ferromanganese, etc. In such processes as the acid and basic open hearths, however, the manganese content of the finished material also depends upon its concentration in the pig iron charged.

Presence of Manganese in Steel

Manganese may be present in steel in several different forms. As will be shown later, manganese is entirely soluble in liquid iron and quite appreciably soluble in solid iron. The largest portion of this material exists in solid or liquid solution as an alloy; however, other forms are present, but to a much lesser degree. Some of the manganese exists as manganese carbide (Mn_3C), probably in conjunction with the iron carbide of similar composition. Other forms in which manganese may exist in steel are such compounds as manganous oxide and manganous sulphide, products of the reactions of manganese with iron oxides and iron sulphides, respectively. The phenomena that accompany the presence of these various forms of manganese in steel will be discussed in the following pages.

Ferrous Alloys of Manganese — Phase Diagrams

Nearly all ferrous alloys of manganese exist in the quaternary system iron-manganese-carbon-silicon, and most of these have compositions in the close proximity of the iron-manganese binary system.

High- and low-carbon ferromanganese and the silicomanganese alloys have compositions near the manganese-rich side of this binary, whereas low- and high-carbon spiegels (and silicospiegels) and the manganese steels are all located near the iron-rich side of the iron-manganese system.

As has been pointed out in various sections of this paper, the manganese-rich alloys are used chiefly as addition agents (deoxidizers, etc.) in steel manufacture. Our main interest in these materials therefore lies in the case and economy with which they can be manufactured and used and not necessarily in their physical properties as alloys.

On the other hand, iron-rich manganese alloys are extremely interesting from the standpoint of their physical characteristics, and one of the following sections is devoted to the properties of the manganese steels.

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In the following pages the available data concerning the six binary and the four ternary phase diagrams constituting the basis for the quaternary system iron-manganese-carbon-silicon are discussed.

Binary Systems

System Iron-Manganese. - The system iron-manganese, as determined by various investigators, is shown in figure 35. The liquidus and solidus are given according to Rumelin and Fick (330) and Levin and Tammann (233), whose values are all in fair agreement. These curves indicate that at high temperatures iron and manganese form continuous series of solid and liquid solutions. The only apparent interruption occurs in the iron-rich side of the diagram and is due to the delta-gamma iron transformation. This portion of the diagram was established by Rumelin and Fick. They found that the melting point of pure iron was 1,528° C., and its delta-gamma transformation occurred at 1,401° C. This transformation temperature is raised by small manganese additions, and between 2 and 10 percent manganese the transformation begins at 1,454 ± 2° C. Above 10 percent manganese the delta-gamma transformation cannot be detected by thermal analysis, and it is believed that alloys containing more than 12 percent manganese solidify with the formation of the gamma solid solution.

Iron-rich alloys. - The effect of manganese on the gamma-alpha transformation in the iron-rich alloys is shown graphically in figure 35. With increasing manganese contents this transformation, which occurs in pure iron at 900° C., is lowered rapidly. This side of the diagram has been studied by various investigators, chiefly Öhman (282), Walters (378), Schmidt (339), Dejean (64), Bain (12), and Ishiwara (177).

In general, all their values are similar. Walters and Öhman probably had the purest alloys and checked their findings by various experimental methods.

The results of these investigations indicate that the lowering of the gamma-alpha iron transformation is characterized by the area ABC in the figure. Above and to the right of this area the face-centered gamma solid solution is the stable phase, whereas below and to the left of this region the body-centered alpha solid solution is stable. Alloys having compositions within this area contain both phases. This immiscibility region is limited at room temperatures by the values obtained by various workers. Point C was established by the work of Öhman (282), Ishiwara (177), Schmidt (339), and Bain (12), whereas point B was established by Bain.

Schmidt's X-ray investigations introduced a rather interesting complication to this portion of the diagram. He found that alloys containing 12 to 29 percent manganese (or within the above mentioned immiscibility range) exhibit a hexagonal close-packed structure. This he called the epsilon phase. Although several other investigators (Öhman, Ishiwara, and Walters) have also identified this phase, there is considerable uncertainty as to its significance. Schmidt suggests that it is a solid solution of iron and manganese which is stable only at low temperatures. Öhman states that this

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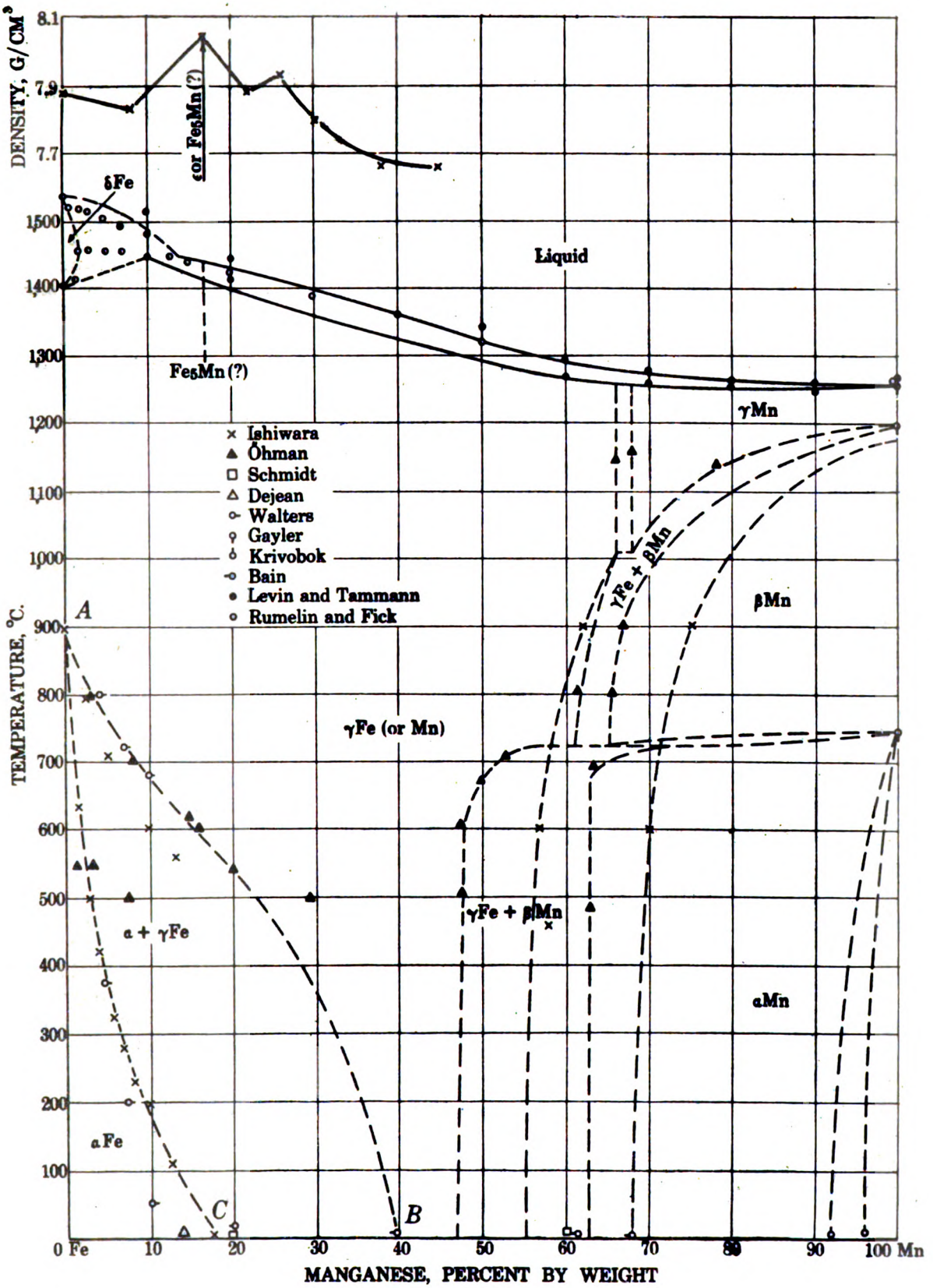

Figure 35.- System iron-manganese.

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phase is not stable over 500° C. and is formed only by the decomposition of the gamma-iron phase and the simultaneous formation of a supersaturated alpha-iron phase. This was termed alpha-prime instead of epsilon (according to Schmidt), and the significance of this term is apparent.

However, the almost simultaneous publication by Ishiwara suggested that the origin of this new phase (epsilon or alpha-prime) was the compound Fe_5Mn, which according to him is stable only at high temperatures. There is little confirmatory evidence in favor of this theory other than his density measurements shown at the top of figure 41. However, Öhman states that the epsilon phase is only stable when rapidly cooled and that the strongest indication of the hexagonal epsilon phase was found in an alloy containing 22.9 atomic percent of manganese and quenched at 1,100° C. The atomic percentage of manganese in Fe_5Mn is 16.66 percent, and the above alloy would contain a large portion of this compound, provided of course that it exists. This question will probably be investigated further by some authors already mentioned herein.

Manganese-rich alloys. - The properties of pure manganese have already been discussed in chapter 1 and will not be repeated. However, for the purposes of this section it should be recalled that manganese exhibits two allotropic transformations (107). Cubic alpha manganese is stable form 0° to 742° C., whereas cubic beta manganese is stable from 742° to 1,191° C. From the latter temperature up to the melting point (1,245° C.) the face-centered tetragonal form (gamma) is stable.

The effect of iron on the manganese transformation has been studied. There is some disagreement in the results of the various investigations, although the general trends are similar. As shown in figure 35, iron rapidly lowers the gamma-beta transformation from 1,191° C. at 0 percent iron to 725° C. at approximately 40 percent iron. Some investigators, such as Ishiwara (177) and Krivobok (219), concluded that the gamma-beta transformation was lowered to room temperature at approximately 40 percent iron. Öhman's investigations, however, indicated that the effect of the beta-alpha manganese transformation was quite apparent. With increasing iron content this transformation was lowered from 742° to 725° C. at 60 percent iron. Hence an alloy containing more than 40 percent iron will transform directly from the gamma (iron or manganese) solid solution into the alpha without passing through the intermediate form of beta solid solutions.

The gamma-beta immiscibility ranges are shown in the figure according to Öhman and Ishiwara. Because of the purity of Öhman's samples his values are probably more correct. Ishiwara plotted the amount of "Manganese added" rather than analytical values, and his conclusions are somewhat questionable.

Öhman also gives the immiscibility ranges of the gamma-alpha manganese solid solutions as ranging from 48 to 63 percent manganese at 500° C. and assumes that nearly the same limits are maintained at room temperature. Bain's limits for this immiscibility region ranged from 61 to 68 percent manganese at room temperature, whereas Schmidt found that the lower manganese limit was at 60 percent manganese at room temperature.

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Krivobok stated that according to his metallographic studies the beta-manganese solid solution was stable at room temperature between 65 and 92 percent manganese. Also, gamma and beta manganese were immiscible between 58 and 65 percent manganese, and similarly the beta and alpha immiscibility range varied from 92 to 96 percent manganese at room temperature. Hence alpha manganese was only stable form 96 to 100 percent manganese or conversely 0 to 4 percent iron. These results have not been substantiated by X-ray studies. According to the above abstracts iron and manganese form complete series of solid and liquid solutions at high temperatures, but due to the various allotropic transformations in both iron and manganese such is not the case at room temperatures.

The X-ray studies of Bain, Schmidt, Öhman, and Ishiwara on iron-manganese alloys at room temperatures have been summarized briefly in the following table:

TABLE 84. - Composition Ranges of Stable Solid Solutions in the Iron-Manganese System

Solid solution	Concentration limits at 25° C., percent manganese	Crystal structure
Alpha iron	0-18	Body-centered cubic.
Alpha + gamma iron[1]	18-39	Body-centered and face-centered cubic.
Epsilon (or Fe_5Mn?)	13-29	Hexagonal close-packed.
Gamma iron	39-47 (or 55)	Face-centered cubic.
Gamma + alpha manganese[1]	47 (or 55) to 63 (or 68)	Face-centered cubic and cubic.
Alpha manganese	63 (or 68) to 100	Cubic 56 atoms per unit cell

1 Two immiscible solutions.

Osawa (285) and Öhman (282) studied the effects of increasing manganese contents on the crystal structure of iron and the effects of iron on the space-lattice constants of alpha, beta, and gamma manganese.

Benedicks (21) studied the effect of manganese on the density of liquid iron at 1,600° C. Only a very slight decrease was noted up to 19 percent manganese.

System Manganese-Carbon. - This is essentially the manganese-manganese carbide (Mn_3C) system, and up to the composition of Mn_3C these two materials are completely miscible in the liquid state. This has been determined by Stadeler (353) whose phase diagram is shown in figure 36. Unfortunately, Stadeler's temperature for the melting point of manganese is some 45° C. lower

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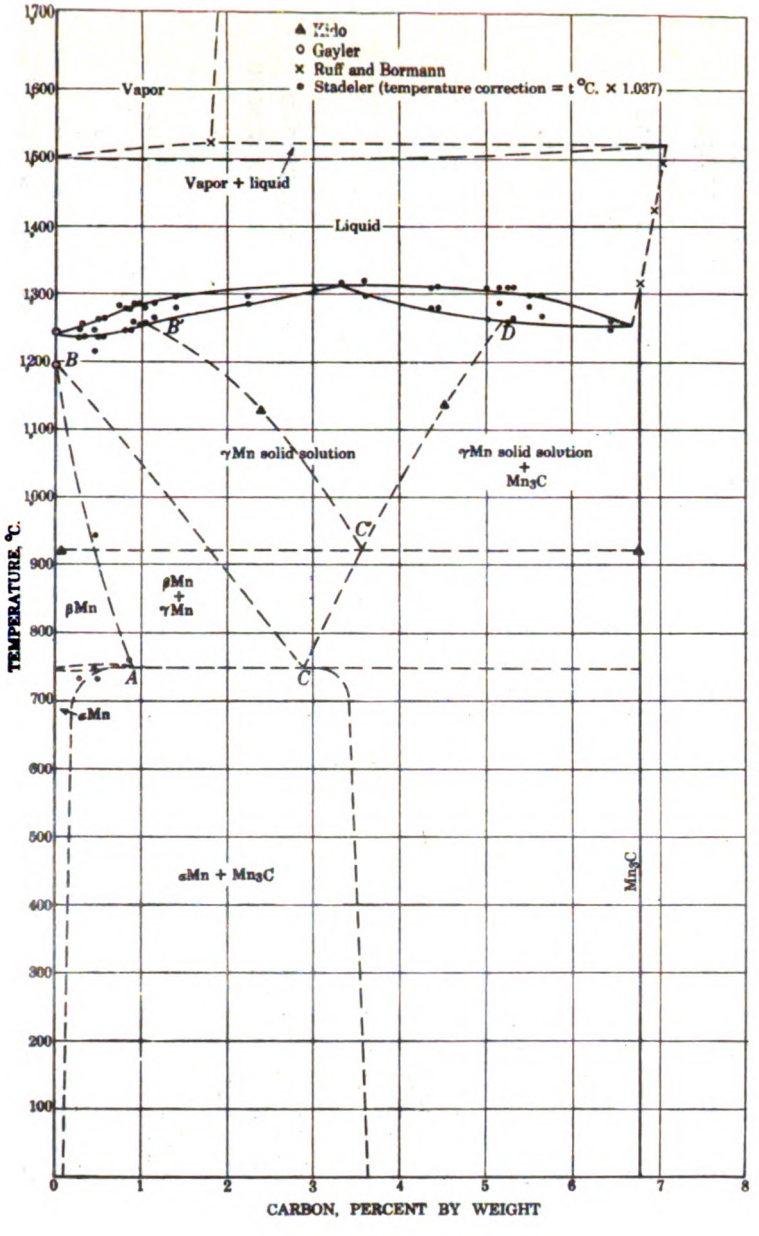

Figure 36.- System manganese-carbon.

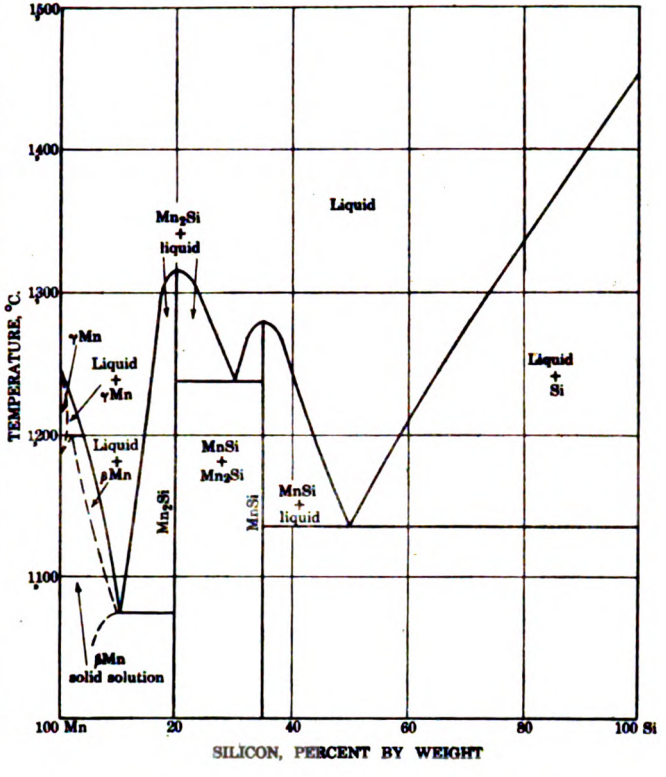

Figure 37.- System manganese-silicon, according to Döringkel.

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than Gayler's (107), and the points plotted in figure 36 have been corrected proportionally for this amount by multiplying by $\frac{1,245}{1,200} = 1.0375$. These plotted values show a liquidus having a maximum temperature (1,315° C.) at about 50 percent Mn_3C (or 3.4 percent carbon). The temperature drops gradually on either side of this point to the melting points of manganese and Mn_3C.

Ruff and Bormann (323) determined the solubility of carbon in liquid manganese at temperatures above the melting point of liquid Mn_3C. Their values, which are also shown in figure 36, accord with Stadeler's corrected values. Ruff and Bormann also determined the boiling points of manganese-carbon alloys, and these data are represented diagrammatically in figure 36.

The characteristics of the solid alloys are not so well-established as in the iron-manganese system. Stadeler determined the limits of the solid solubility of Mn_3C in manganese and conversely manganese in Mn_3C, and stated that solid alloys bounded by the points 0.1 percent C, A, C, and 3.6 percent C are composed of two immiscible solid solutions, one of which is manganese-rich whereas the other is carbide-rich.

Kido (202) studied Mn-Mn_3C alloys by thermal means and concluded that the system contains a eutectoid (C in figure 36). According to Kido the region B'C'D of figure 36 contains the homogeneous solid solution of gamma manganese in Mn_3C. Alloys left of line B'C' contain two phases, gamma manganese and the above solid solution. Alloys right of line C'D are composed of two phases, the solid solution and the carbide.

The eutectoid temperature (920° C.) was supposed to be approximately the same as the beta-alpha manganese transformation. This however is not the case, as was shown previously. This transformation takes place at 742° C. If we assume that there is a eutectoid in the system and correlate this assumption with Stadeler's results, it is possible to construct a much more reasonable diagram, such as that indicated by points A, B, C, and D.

This system extends the gamma-manganese solid solution over to the gamma-beta transformation in pure manganese at point B. The eutectoid temperature and composition represented by point C agree very well with Stadeler's immiscibility range described above. Likewise his values agree favorably with point A, which has been taken as the limiting solubility of Mn_3C in beta manganese at the beta-alpha transformation.

Other points of Stadeler's that agree with this diagram are the following: 4.5 percent C, 940° C.; 12.5 percent C, 960° C.; and 3.6 percent C, 887° C., all of which are shown in the figure. Because of the uncertainty of the solid solubility limits all lines have been dotted in the figure.

At present these alloys have but little practical use, but the system Mn-Mn_3C has great theoretical interest because it confirms the existence of Mn_3C -- an item of great importance to ferrous metallographists.

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Ferromanganese is the only practical alloy having compositions approximately within this system. High-carbon ferromanganese is essentially a mixture of iron and manganese carbides ($Mn_3C + Fe_3C$), inasmuch as it contains about 7.5 percent carbon, 80 percent manganese, and 12.5 percent iron. There are probably only infinitesimal amounts of uncombined iron or manganese present. Low-carbon ferromanganese, containing 2 to 3 percent carbon, 80 percent manganese, and 17 to 18 percent of iron, probably contains a large percentage of the eutectoid represented by point C, figure 36.

System Manganese-Silicon. - According to the specific-gravity determinations of Frilley (100), four silicides of manganese should exist -- Mn_2Si, $MnSi_2$, MnSi, and Mn_5Si. However, other researches have identified only two -- Mn_2Si and MnSi. The existence of these two silicides has been confirmed by the melting-point work of Dörinckel (74), whose results are shown diagrammatically in figure 37. The only change in his values which has been made in constructing this diagram is the melting point of silicon. This has been plotted at 1,458° C., according to the selected value given by Mellor (252).

No account has been made by Dörinckel of the gamma-beta manganese transformation, and for this reason the tentative break in the solidus of the high-manganese alloys has been made. This is given in a manner similar to the delta-gamma iron transformation shown in the system iron-manganese (fig. 35).

Little is known about the physical properties of these alloys at room temperatures. In fact, the analyses of few if any commercial alloys are to be found strictly within this binary system. The more practical alloys at present are to be found within the quaternary system iron-manganese-silicon-carbon.

Other Binary Diagrams in Quaternary System Iron-Manganese-Carbon-Silicon. - The following manganese-free binary systems are given briefly herein because of their importance in connection with manganese alloys.

System iron-carbon. - This system is so well known that it will not be discussed in detail herein. The equilibrium diagram is reproduced in figure 38 according to the selected values by Ralston (310). This figure might more appropriately be called the system Fe-Fe_3C. A recent publication by Körber and Ölsen (212) is particularly interesting, inasmuch as they have represented in one diagram nearly all of the experimental data pertaining to this system. As shown in the figure, this system includes one eutectic and one eutectoid as contrasted with the Mn-Mn_3C system, the liquidus of which exhibits a maximum with no compounds or eutectics. As stated in the above discussion, however, the latter system may contain a eutectoid. The connection between this and the Mn-Mn_3C system will be discussed in connection with the ternary diagram iron-manganese-carbon.

System iron-silicon. - The system iron-silicon, as shown in figure 39, was constructed according to the diagrams given by Mellor (253) and the International Critical Tables (176). Except for a few discrepancies in temperatures the two systems described by these authorities are the same up to about 40 percent silicon. The $FeSi_2$ solid-solution (epsilon) range was

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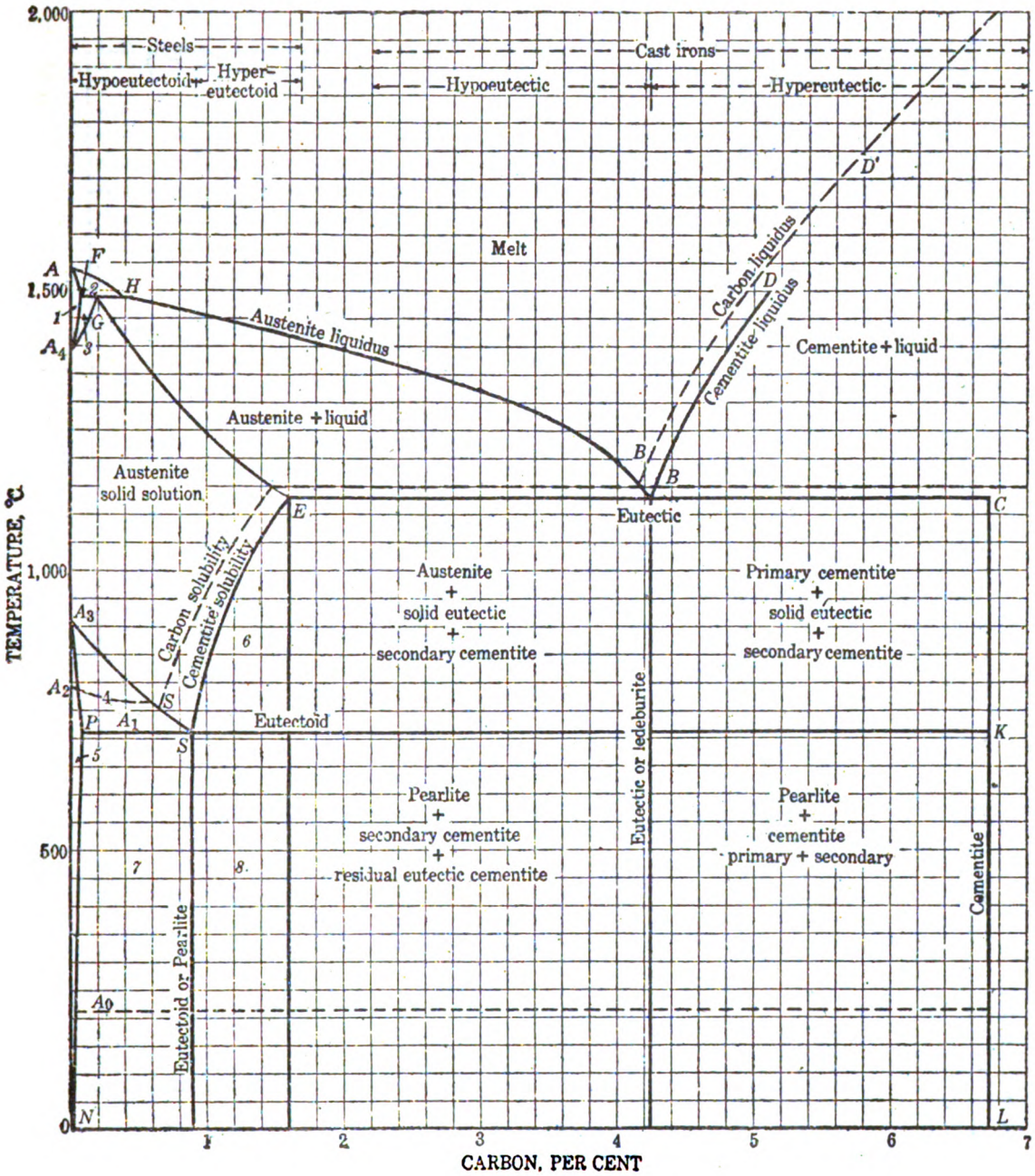

FIGURE 38.—Iron-carbon temperature-composition phase diagram: Area *1*, δ ferrite, maximum solubility of carbon 0.07 per cent; area *2*, δ ferrite + melt; area *3*, δ ferrite + austenite; area *4*, α ferrite + austenite; area *5*, α ferrite, maximum solubility of carbon 0.034 per cent; area *6*, austenite + proeutectoid cementite; area *7*, proeutectoid α ferrite + pearlite; area *8*, proeutectoid cementite + pearlite. Point A_0, temperature of magnetic transformation of Fe_3C, 210° C.; point A_1, temperature of eutectoid (splitting of solid austenite into α ferrite and cementite), 720° C.; point A_2, temperature of magnetic transformation of α ferrite, 795° C.; point A_3, temperature of transformation of γ ferrite to α ferrite, 906° C.; point A_4, temperature o ftransformation of δ ferrite to γ ferrite, 1,400° C.; point *A*, melting point of pure iron, 1,535° C.; point *N*, solubility of carbon (as cementite) at room temperature, 0.003 per cent C.

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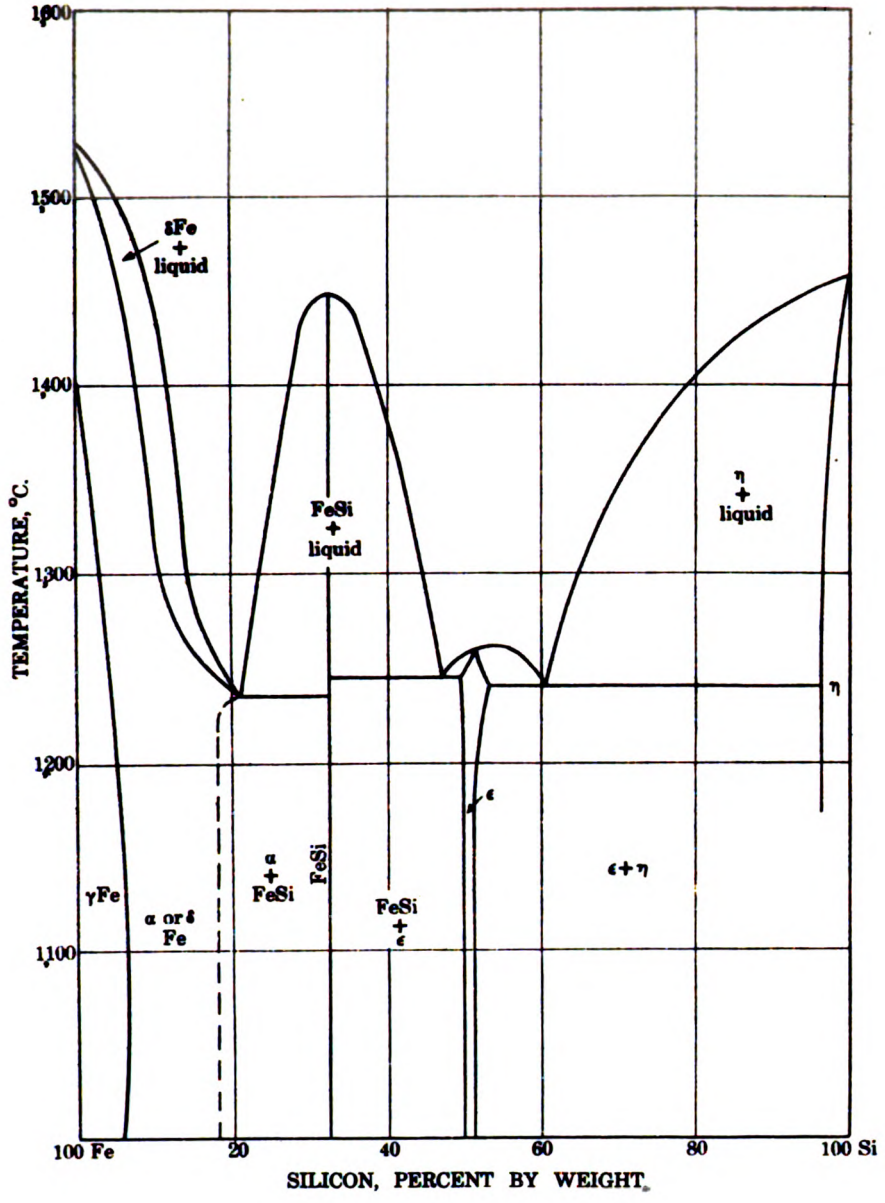

Figure 39.- System iron-silicon.

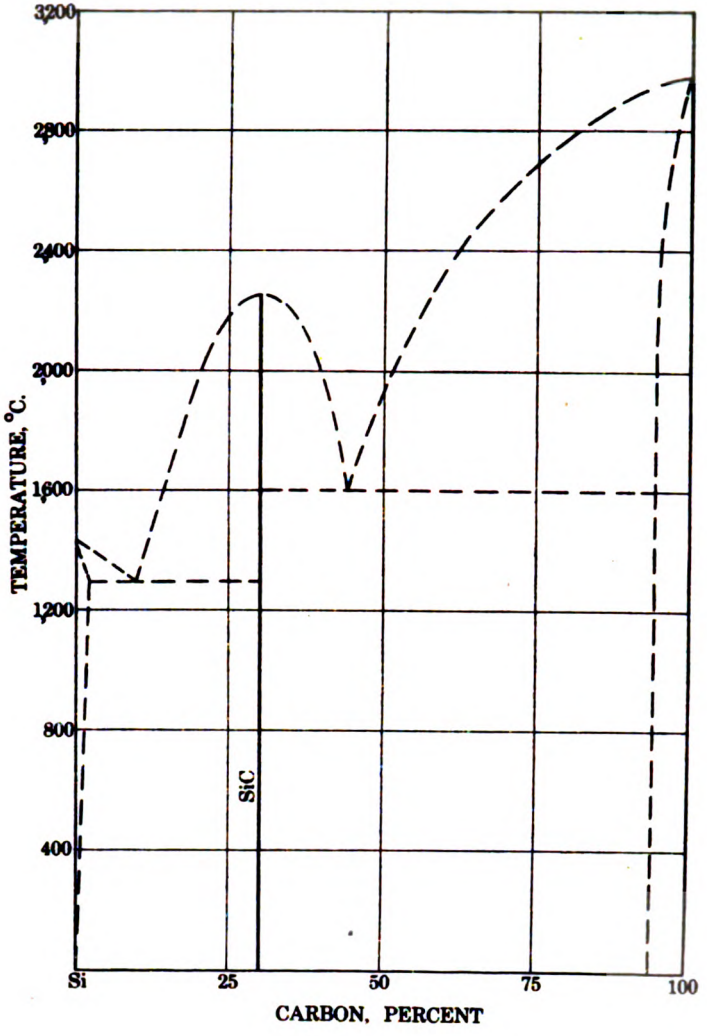

Figure 40.- Tentative system silicon-carbon.

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not given by Mellor; likewise the range of the γ-solid solution was not considered by this author. The melting point of silicon was given according to Mellor's previously mentioned "selected" value -- 1,458° C.

The discrepancies between these two publications are probably due to the literature to which they referred. Neither referred to work cited by the other.

The data considered by Mellor were obtained by Murakami (268), Gontermann (119), Lowzow (235), Kurnakoff and Urasoff (223), and Guertler and Tammann (127). The diagram given by the International Critical Tables was constructed according to the works of Grüneisen (125), Herz (160), Johnston and Adams (181), and Cohen and Helderman (54).

The correlation of this system with the system iron-silicon-manganese will involve discussions of greater interest for the purposes of this paper than a complete discussion of this binary, at this time.

System silicon-carbon. - Because of the extremely high temperatures involved very little is known about this system. There is little question, however, as to the existence of the compound SiC (carborundum), which was first discovered by Schützenberger (344). This compound has a high melting point (2,227° C.), according to the estimates of Weigel (382). The existence of two other compounds has been suggested. Silicon dicarbide (SiC_2) was supposed to have been prepared by Colson (56), whereas Kohn-Abrest (251) believed he had prepared C_5Si_3. The existence of these compounds has not been checked by subsequent investigations. These two latter investigators may have obtained a eutectic in the system silicon-carbon, which was composed of SiC and C.

If such were the case this system would have the appearance of the very tentative diagram in figure 40. The melting points of silicon, SiC, and carbon are all known with a fair degree of accuracy (that is, 1,458°, 2,227°, and 3,000° C. respectively), and these values have been used in constructing this tentative diagram. The compositions of the two compounds SiC_2 and Si_3C_5 are 46.2 and 41.6 percent carbon, respectively. By assuming that the discoverers of these two compounds really were dealing with a eutectic, the eutectic composition was taken as the mean of these two compositions. The eutectic temperatures have both been assumed in constructing this diagram.

The above assumptions have been made for the purpose of studying the ternary and quaternary systems involving this binary. This is the only binary that is not known with fair accuracy.

Ternary-Phase Diagrams in Quaternary System Iron-Manganese-Silicon-Carbon

There are four possible ternary diagrams in the quaternary system under consideration -- the systems iron-manganese-carbon, iron-silicon-carbon, iron-manganese-silicon, and manganese-silicon-carbon. Unfortunately, no information was found applicable to the latter two systems. Furthermore, only small areas in the first two systems have been investigated. Certain attempts have been made to extrapolate the influence of the various binary

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systems into the ternary, but these studies will not be given herein. Such extrapolation has most often led to erroneous conclusions.

The determination of the liquid- and solid-phase equilibria in all four systems should represent an excellent field for fundamental research.

The effects of manganese and silicon on the solubility of carbon in iron have been determined and will now be discussed under the headings "The System Iron-Manganese-Carbon" and "The System Iron-Silicon-Carbon." The data are too meager, however, to establish these systems completely.

System Iron-Manganese-Carbon. - Manganese increases the solubility of carbon in iron, according to Wüst (398). His data show that a sample containing 0.06 percent manganese can hold only 4.28 percent carbon in solution. With 4.23 percent manganese, 4.97 percent carbon can be present, whereas with higher percentages of manganese — 12.66, 59.73, and 80.45 — the melt can contain 5.38, 6.76, and 6.90 percent carbon, respectively.

The freezing points of nearly all Wüst's samples were virtually at the same temperatures (1,120° to 1,146° C.) in most instances. Probably these temperatures really represent the freezing point of a ternary eutectic. If this is true Wüst merely determined the temperature at which the last portions of his melts solidified on cooling, or the first portions became liquid on heating. The above-mentioned carbon solubilities are therefore indeterminate because the fourth variable, temperature, was unknown.

The tendency for manganese to increase the solubility of carbon in liquid iron was also observed by Nordbury (276), Goerens (115), and Kürten (225). The latter author stated that ferromanganese can contain as much as 7.5 percent of carbon, an observation often made with regard to this material.

Oberhoffer (278) reviewed the work of Lütke and concluded that ternary alloys included in an area formed by drawing lines between the points manganese, 0 percent, carbon, 1.8 percent; manganese, 35 percent, carbon, 3.5 percent; and manganese, 0 percent, carbon, 6.67 percent contained two heterogeneous phases at room temperature. One phase was iron-rich, whereas the other was carbon (or carbide) rich; also the alloys within this range of composition were not malleable.

System iron-silicon-carbon. - Wüst (398) observed that when silicon is added to low-manganese pig iron carbon is precipitated from the liquid. The eutectic composition (in the system iron-carbon) decreased from 4.3 percent with low silicon to about 0.87 percent when 27 percent silicon was added. Other investigators who observed this effect in liquid melts were Charpy and Cornu (46), Andrew (8), and Honda and Murakami (166).

Gontermann (119) determined the primary crystallization temperatures of low-silicon alloys (up to 10 percent silicon). Isotherms plotted from his experimental data clearly indicate the above-mentioned carbon-solubility-reducing tendency of silicon. The solidus in nearly every sample was in the same temperature range (1,076°-1,168°) and most of these

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temperatures ranged only from 1,121° to 1,150°, an average of 1,135° C. This is probably the freezing point of a ternary eutectic.

Various investigators studied the effect of silicon on the solubility of carbon in solid iron. Chief among these were Charpy and Cornu (47), Becker (18), Hanson (146), Pearson (299), Yensen (402), and Kriz and Poboril (221). Their data are not adequate, however, for constructing the ternary system.

Quaternary System Iron-Manganese-Silicon-Carbon

In spite of the greater number of variables in this system, considerable information has recently been made available through the investigations of Herty and Royer (157). It is rather difficult to vision a four-component system, but the picture can be simplified in this particular instance by stating that the above authors determined the solubility of carbon in iron-manganese-silicon alloys at specified temperatures. This may be clarified further by reference to their diagram reproduced in figure 41. The base of this figure is the ternary system iron-manganese-silicon, whereas the vertical axis represents the carbon concentration in the saturated alloy. The curved surface represents the saturated-carbon content of all alloys at 1,700° C., and its limits are represented as follows:

TABLE 85. - Limiting Carbon Contents in System Fe-Mn-C-Si

Alloy:	Percent C, Saturated
100 percent Mn	7.84
100 percent Fe	5.90
42 percent Mn, 58 percent Si	.00
46 percent Fe, 54 percent Si	.00

A similar but lower (concentric) curved surface would be obtained by graphic representation of the carbon saturation values at lower temperatures (1,300° and 1,500° C.).

It is obvious from figure 41 and table 85 that manganese overcomes the carbon-precipitation tendencies of silicon more than iron. For example, 58 percent of silicon is required to decrease the carbon solubility to zero in a manganese-silicon alloy, whereas 54 percent is required to prevent carbon solubility in an iron-silicon alloy. The greater solubility of carbon in manganese than in iron is also shown in the table and figure, manganese dissolving some 2 percent more carbon than iron at 1,700° C. Extrapolation of the solubility curve to 100 percent manganese was necessary, but an experimental iron-manganese melt containing 80 percent manganese was saturated with 7.14 percent carbon at 1,500° C. Iron is saturated with 5.40 percent carbon at the same temperature.

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The graphitizing action of silicon was verified in the above experiments and is indicated by the insolubility of carbon in high-silicon, ternary alloys. The insolubility range varies from iron-silicon alloys containing more than 54 percent of silicon, to manganese-silicon alloys containing more than 58 percent of silicon.

The practical significance of this work may best be illustrated by figure 42, wherein the triangular base of the quaternary system is represented. The limiting iron, manganese, and silicon contents of the present commercial alloys have been represented without respect to their carbon contents.

The manganese steels are represented as being on the iron-manganese binary line. Actually these materials contain less than 0.2 to 0.3 percent silicon. These materials are not so important with regard to carbon saturation, because care is taken to maintain the unsaturated condition. The carbon content of these steels is seldom greater than 1.0 percent, whereas the saturation values represented in figure 41 range from about 5.4 to about 6.3 at 1,500° C.

The analyses of ordinary spiegel and ferromanganese are represented in areas adjacent to the iron-manganese binary because these materials usually contain 1 to 3 percent silicon. The carbon-saturation values for these materials are important and may be estimated by reference to figure 41.

The special steel-deoxidizing alloys (the silicospiegels and silicomanganese) such as those developed recently by Herty and Fitterer (152) are represented according to their analyses in figure 42. The carbon-saturation values for these materials may be estimated by reference to figure 43, which also has been reproduced from Herty and Royer's work. These concentrations were determined by intersecting the solid figure 41 by two planes intersecting the base (shown in fig. 42) at lines AB and AC.

Unless it is otherwise specified, spiegel, silicospiegel, silicomanganese, and ferromanganese are usually saturated with carbon at the manufacturing temperature in accordance with these figures. Occasionally a low-carbon alloy is desirable for addition to low-carbon steel, and unsaturated alloys are requested. Low-carbon ferromanganese, for example, contains only 1 to 2 percent carbon. When such materials are added to low-carbon steels it is not so difficult to meet the manganese and carbon specifications for the heat.

The saturation of carbon in the ferrosilicons can also be estimated according to their limiting analyses plotted in figure 42 and the carbon saturation in figure 41. It will be readily seen that the carbon solubility in such materials is quite low.

The diamond at the top of figure 42 represents the analyses (except for carbon) of the ordinary pig and cast irons. A more complete representation of this diamond on a greatly magnified scale would be very interesting, but it is not important for the purposes of this paper.

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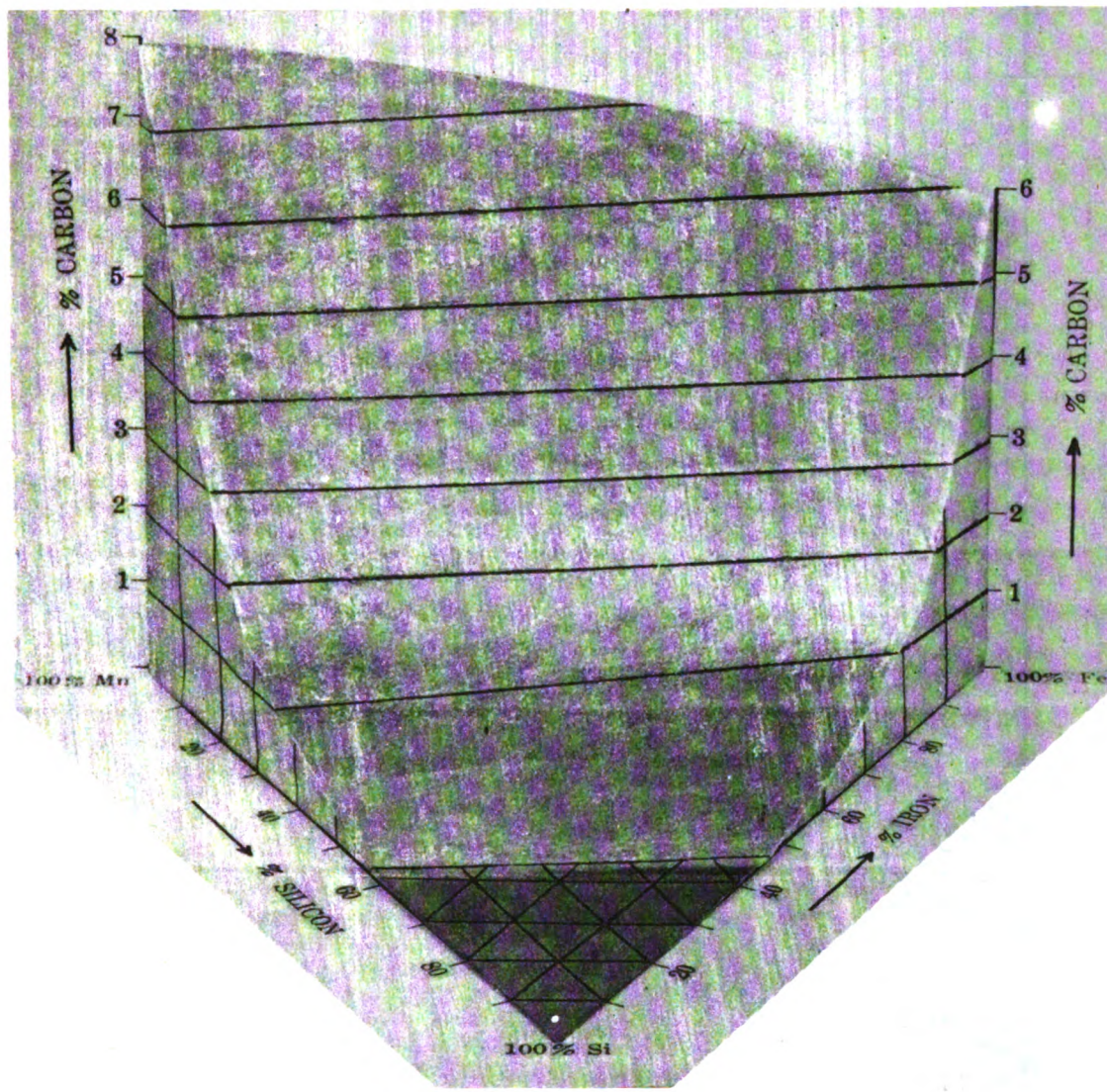

Figure 41.- Carbon solubility at 1,700 C. in Fe, Mn, and Si alloys.

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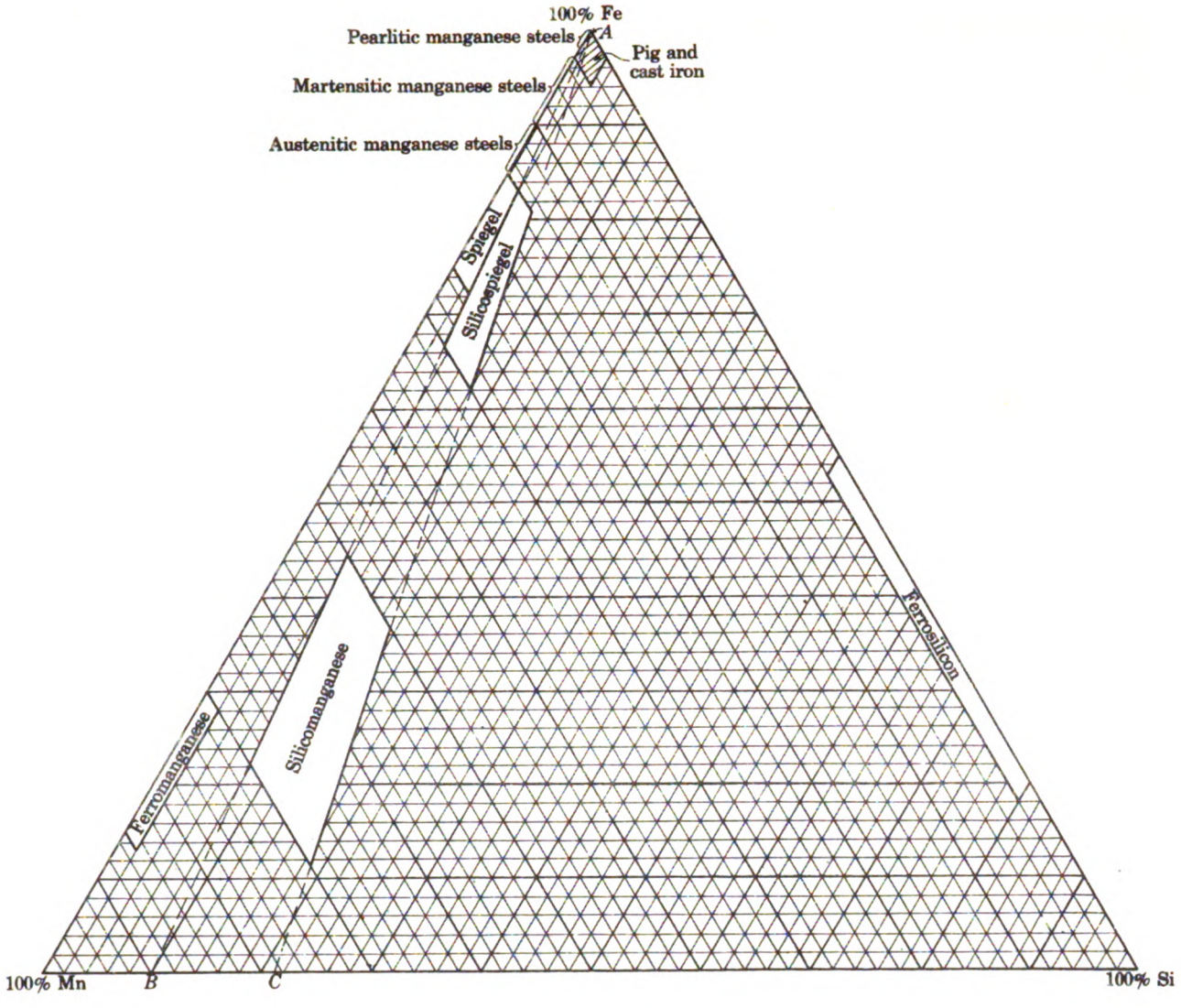

Figure 42.- System iron-manganese-silicon.

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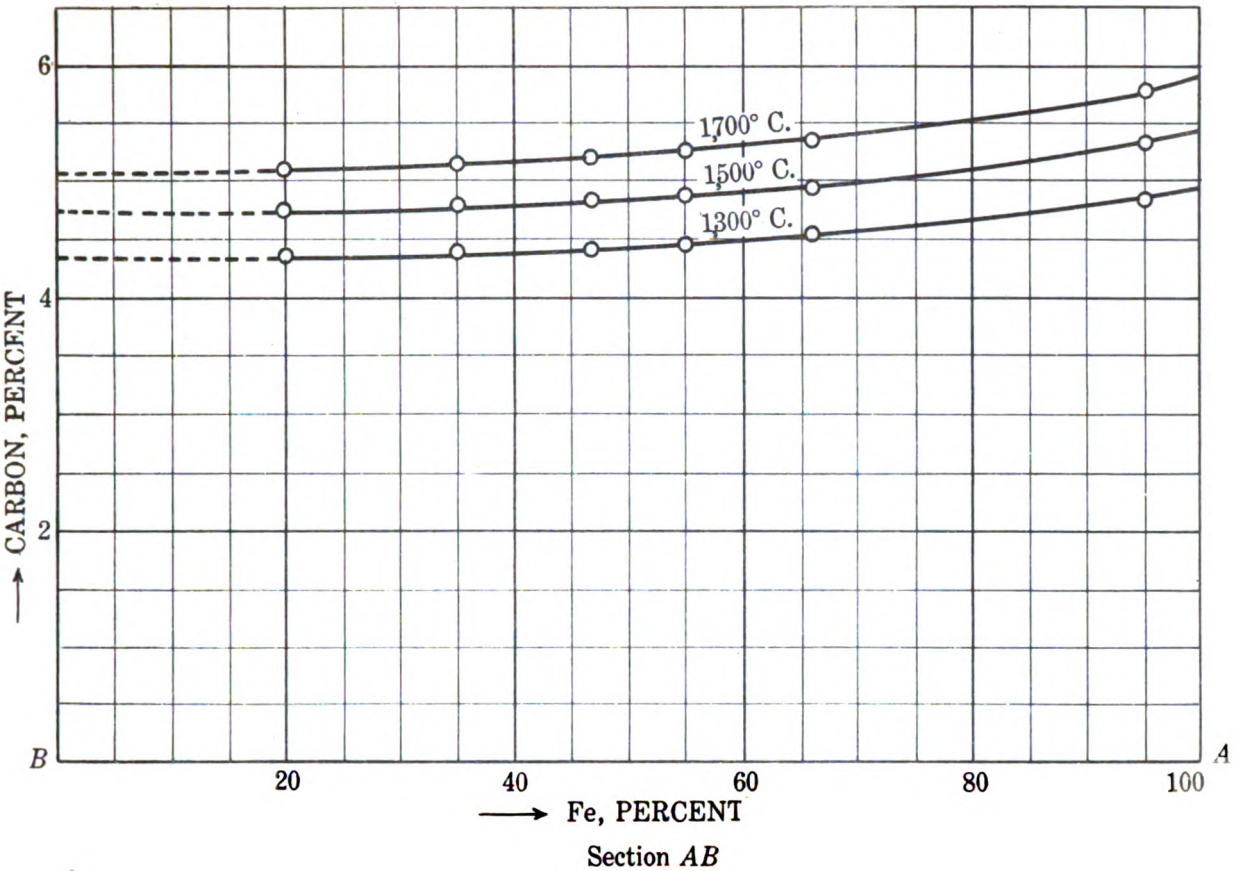
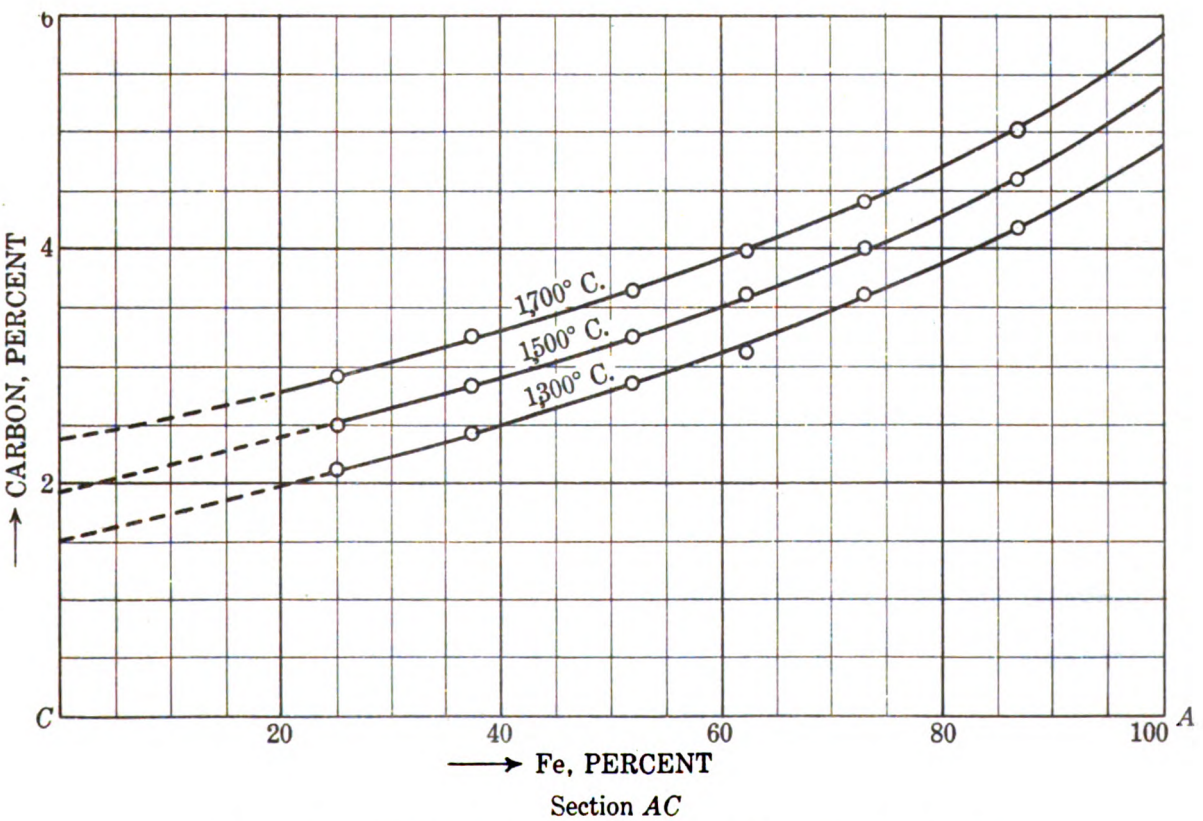


Section *AB*



Section *AC*

Figure 43.- Solubility in sections AB and AC of ternary system.

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Manganese Reactions in Basic Open-Hearth Furnace

From 1924 to 1929, when steel production increased to as much as 56 million gross tons per year, more than 80 percent was the product of the basic open-hearth furnace. During this period, also, the ratio of pig iron to scrap in the charge was reduced from approximately 1.0 to 0.6. In other words, the open hearth became a greater scrap-melting process, and it was found that higher contents of manganese in the pig iron were required. In consequence, the percentage of manganese in basic pig was increased from approximately 1.0 to 2.0 percent. Other factors causing this increase were the use of higher-sulphur ores and higher-sulphur coking and producer coal (390), and by using higher-manganese pig irons the open-hearth operator was insured lower sulphur contents of his finished product. This will be discussed later, on page 281.

When high-manganese pig iron is used higher residual manganese exists throughout the heat, reducing the amount of ferromanganese required at the end of the heat. This increase in the manganese content of pig iron was indicated by the increased concentration of MnO in basic open-hearth slags (151). Slags analyzed in 1917 were compared with those analyzed in 1927, and it was shown that the average manganese content of this type of slag increased from approximately 5 to 8 percent during this period. This loss in manganese through the slag medium has caused considerable comment concerning the conservation of manganese in this country, and this fact will be considered briefly later.

In the basic open-hearth process steel is made by melting scrap, large portions of liquid pig iron generally being added. In some localities where blast furnaces are not used in conjunction with the open-hearth department solid pig iron is charged with the scrap. The more general practice, however, is to add liquid pig iron during the first few hours of the heat. At this time a very complex slag is formed, which may be considered as essentially a calcium silicate containing variable proportions of MnO, FeO, MgO, and small amounts of Al_2O_3, P_2O_5, and sulphur, probably in the form of either or both calcium and manganese sulphides.

The chief reactions into which manganese enters during this process are as follows:

$$FeO + Mn \rightleftarrows MnO + Fe$$
$$FeS + Mn \rightleftarrows MnS + Fe$$

Because of the complex nature of the above slag exact determination of the characteristics of these reactions in the open-hearth process has baffled most attempts for solution. However, many phenomena involving manganese reactions may be qualitatively analyzed by studying the analyses of slag and metal samples taken from charge to tap of a specific open-hearth heat. Some of these phenomena will now be described.

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In a certain heat in a 100-ton stationary open-hearth furnace complete tests were taken during the charging, refining, and tapping periods (195). The analyses of all samples are plotted in figure 44, and the variations with time are recorded therein. One hundred seventy-five thousand pounds of rail steel scrap were charged into the empty furnace, and as soon as possible liquid-steel samples were taken from the melted portion of the charge. Soon thereafter two liquid pig-iron charges were made, weighing 23,000 and 57,540 pounds, respectively, in the order added. The steel scrap contained 0.84 percent manganese, whereas the pig iron contained an average of 1.37 percent. Because the characteristics of manganese reactions can be explained only by plotting the variation of manganese content of the steel with time, the concentrations of carbon and silicon in the metal and of MnO, FeO, SiO_2, and CaO are also shown in figure 44. After the second addition of liquid pig iron most of the scrap had melted, and the liquid portion of the charge contained approximately 1.1 percent manganese. It can be seen from the curve that the MnO content of the slag was greatly increased by the pig-iron addition, inasmuch as its value changed from 14 percent before the addition to 16.5 percent immediately thereafter.

From this time on, as represented by 12:20 o'clock on the figure, the carbon, manganese, and silicon contents of the liquid metal changed quite rapidly with time. Because of the great affinity of silicon for oxygen, the silicon content of the bath was decreased from 0.83 to practically 0.0 percent between 12:20 and 2:00. The carbon content also decreased very rapidly during this period, from 3.6 to 1.5 percent. The elimination of manganese was somewhat slower than either of these two materials, since it only decreased from 1.1 to 0.7 percent. The plotted MnO content of the slag is somewhat deceiving at this time. Although the manganese content of the metal decreased, the MnO content of the slag also decreased. This can be readily explained by the fact that at this time the slag volume was increasing rapidly. Not only did SiO_2 go into the slag due to the elimination of silicon from the metal, but also the limestone charged beneath the scrap at the beginning of the heat started to calcine and rise to the slag phase, thereby diluting the manganese oxide concentration. It is during this period that the so-called flush slags are obtained in open-hearth practice. The volume increases until the slag overflows the furnace bank at some determined spot. A discussion of the recovery of manganese from flush slags has been given on page 109. Elimination of 0.8 percent silicon in the charge would account for as much as 2,000 pounds of SiO_2 in the slag. Probably a similar amount of lime reached the slag phase during this period.

From 2:00 to 5:00 o'clock the manganese concentration in the metal decreased from 0.7 to 0.57 percent. Elimination of this amount of manganese in the metal was reflected in the increase in the MnO concentration of the slag from 10 to 15 percent. It was probably indicated in this manner, because the slag volume during this period was fairly constant. The carbon content of the metal decreased from 1.5 to 1.25 and held fairly constant until 5:00 o'clock. At this time two rather large additions of iron ore were made (a total of 7,000 pounds) to reduce the carbon content to specification limits. Immediately after these additions the manganese

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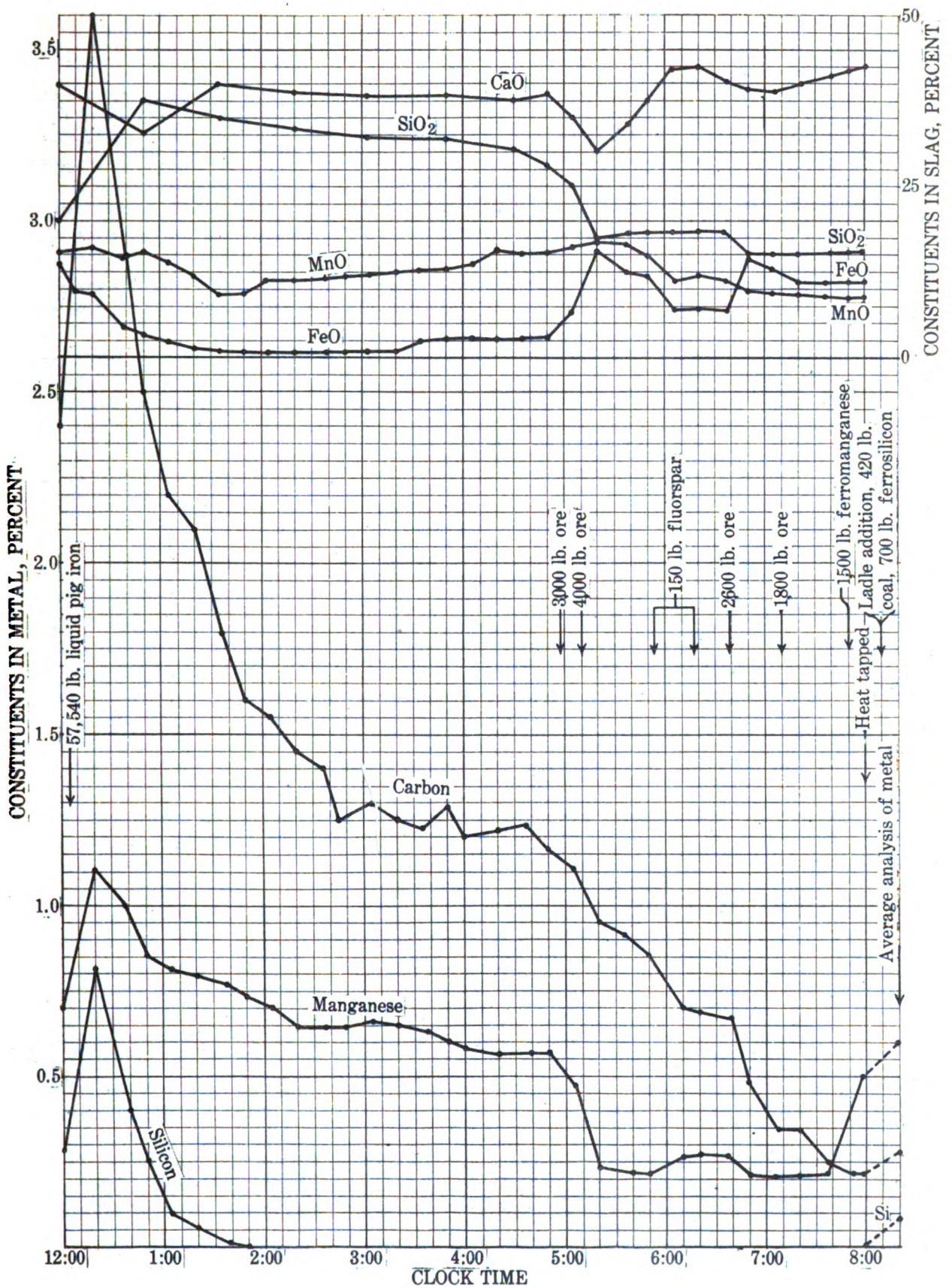

Figure 44.- Manganese reactions in the basic open-hearth furnace (Keats and Herty).

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and carbon concentrations dropped sharply from 0.57 to 0.24 and from 1.25 to 0.95, respectively. These ore additions were indicated in the analysis of the slag by reduction of the percentages of all constituents but FeO and MnO. The FeO concentration increased sharply, whereas the CaO and SiO_2 concentrations decreased rapidly. The concentration of the first oxide was obviously increased by means of the ore addition, whereas the reductions in CaO and SiO_2 were very probably due to dilution of the slag with iron oxide. In spite of this dilution the MnO concentration increased somewhat because of the oxidation of manganese in the metal.

During the next half-hour period between 5.45 and 6.15, 150 pounds of fluorspar were added to the slag. This material, as is well known, can reduce the viscosity of the slag to a considerable extent. The slag, previously very viscous, soon became quite liquid and either caused some lumps of lime to dissolve in the slag or eroded the walls of the furnace and thereby increased the CaO concentration of the slag. Again, the effect of dilution is indicated by a decrease in the MnO and FeO contents of the slag. For some unexplained reason the SiO_2 content held fairly constant.

At the end of this period an increase in the manganese content of the slag was found, which may be due to 1 or 2 factors or both, namely, a change in temperature, or the above-mentioned increase in the basicity (CaO content) of the slag. At 6.40 and 7.10, 2,600 pounds and 1,800 pounds of ore respectively were added. The effects of these additions on the analyses of the slag and metal are indicated only by an increase in the manganese content of the metal and the usual dilution effect of the slag constituents, namely, a decrease in all constituents other than FeO and an increase in the concentration of this material. A marked decrease in carbon content was also observed.

At this time the usual melter's break test was taken, and it was decided that the carbon content had reached the desired value; 1,500 pounds of ferromanganese were added at 7.52 and the heat tapped at 7.58. Tests taken during this short period indicated the expected rise in manganese concentration from 0.25 to 0.49 percent. No manganese in any form was added to the ladle. Instead, coal and ferrosilicon were added for recarburizing and deoxidizing. The average analysis of the heat, as determined by sampling various ingots, was: Manganese, 0.60 percent; carbon, 0.27 percent; and silicon, 0.08 percent. The increase in manganese observed between the tapping test in the furnace and the average analysis of the heat may be due to one of two things — better distribution of the ferromanganese added just before tapping or the reduction of MnO in the ladle slag by means of the silicon and coal additions. It is very probable that both of these effects increased this value.

Various basic open-hearth heats have been described in a manner similar to the above, but more complete tests and more normal reactions of manganese were experienced in this heat than in various other published works.

Manganese Reactions in Acid Open-Hearth Furnace

In the acid open-hearth furnace the steel bath is in contact from charge to tap with a slag composed chiefly of MnO, FeO, and SiO_2. A rather complete

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study (392) has been made of acid open-hearth slags, particularly those which have been cooled slowly. The mineral constituents of the slags after crystallization have been found to be tridymite (SiO_2), cristobalite (SiO_2), fayalite ($2FeO \cdot SiO_2$), and rhodonite ($MnO \cdot SiO_2$). The silica phases crystallize first on cooling, followed by fayalite and rhodonite, the latter two depending upon the ratio of FeO and MnO. When this ratio exceeds 2.7 fayalite is formed. In all other cases rhodonite is the constituent precipitated.

In virtually every heat on which analyses have been recorded the SiO_2 content of the slag varies little and is approximately 55 to 60 percent. The MnO and FeO contents seem to be more or less interchangeable and range from 10 to 20 or 25 percent of either constituent. The system FeO-MnO-SiO_2 (152) indicates that SiO_2 is saturated at 1,600° C. with either 35 percent MnO or 40 percent FeO. An equal mixture of FeO and MnO would then saturate SiO_2 at approximately 37.5 percent (FeO + MnO).

A rather complete heat has been described by De Mare (66), and the analyses are plotted in figure 45 against clock time. In this particular heat 141,000 pounds of material—35 percent pig iron and the remainder scrap—were charged to the furnace. The average analysis of the charge as calculated is given by the first points in figure 45. The manganese, silicon, and carbon contents of the charge were quite high in this particular instance, the average analysis being 1.75, 0.64, and 1.7 percent, respectively. During the melting period steel scrap was unquestionably oxidized rather thoroughly, and by the time all the charge had melted these constituents had been reduced appreciably, as shown in the figure, the manganese being down to 0.20 percent, the silicon to 0.07 percent, and the carbon to 1.15 percent. Immediately after melting down a small charge of limestone was added.

The iron-ore addition at 4:50 o'clock had little effect on the manganese and silicon contents but increased the rate of carbon elimination. The temperature at this time was quite high, because within a few hours the carbon continued to be eliminated in spite of the fact that both the manganese and silicon contents increased. This condition is quite normal in acid open-hearth practice and bears out the contention of various experimenters that at the higher temperatures the carbon reaction may continue, whereas the silicon and manganese reactions are reversed. The ore addition had little effect upon the iron oxide content of the slag, probably because the furnace lining was immediately eroded to such an extent that more slag was formed as ferrous silicate. This is borne out by the fact that the MnO content of the slag decreased, whereas the SiO_2 content increased at this time.

The reduction of manganous oxide in the slag increased until 9:10, when the oil and air were shut off and a slight increase in manganese oxide in the slag was indicated. This was probably due to the decrease in the silica content of the slag, as shown in the upper curve, resulting from a decrease in temperature and precipitation of solid silica from the iron-manganese silicate slag. At 9:45 a ferromanganese addition was made which increased the manganese content of the metal from 0.25 to 0.75 percent. The carbon content was increased slightly by means of this addition, due to the carbon content of

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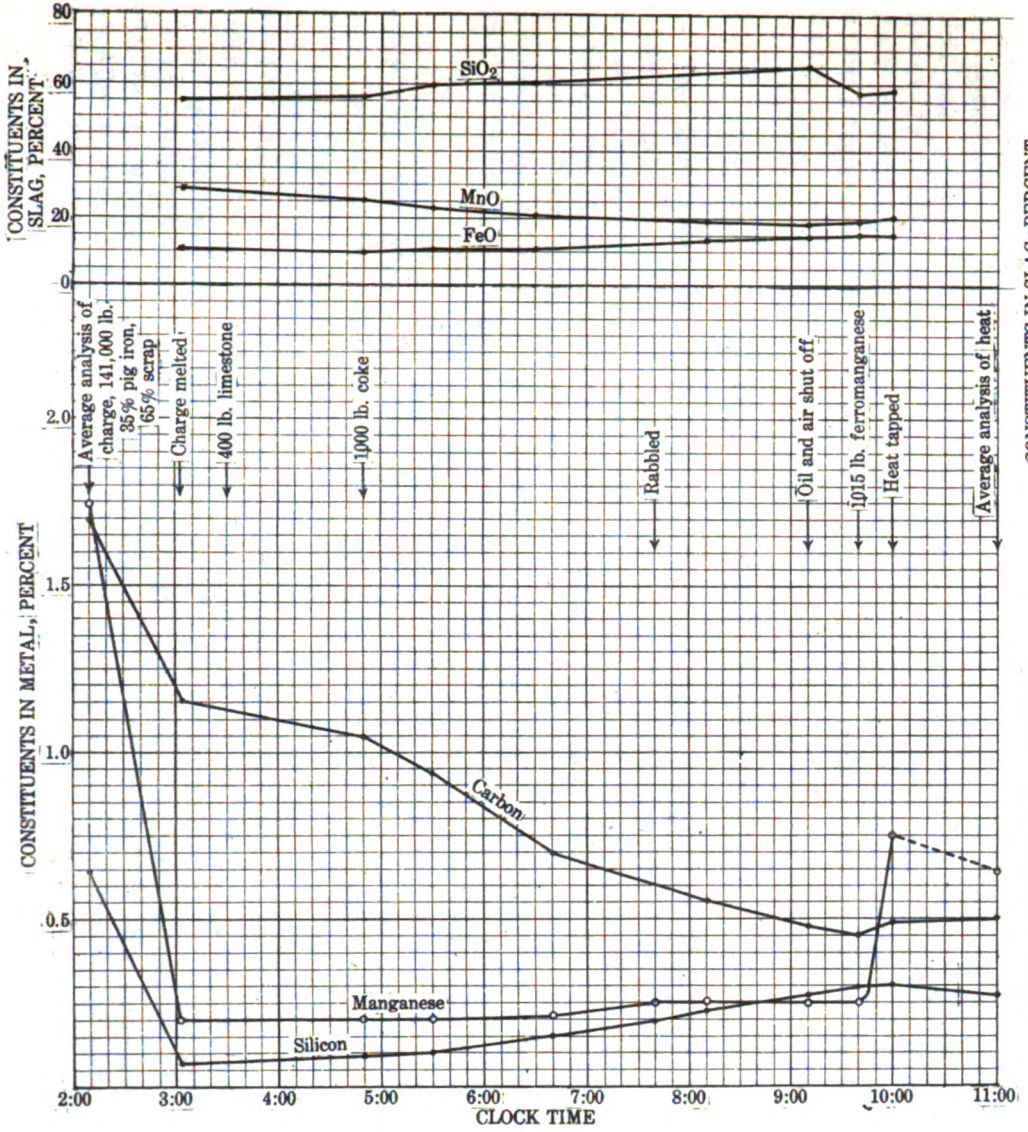

Figure 45.- Analysis of steel during acid open-hearth manufacturing process (De Mare).

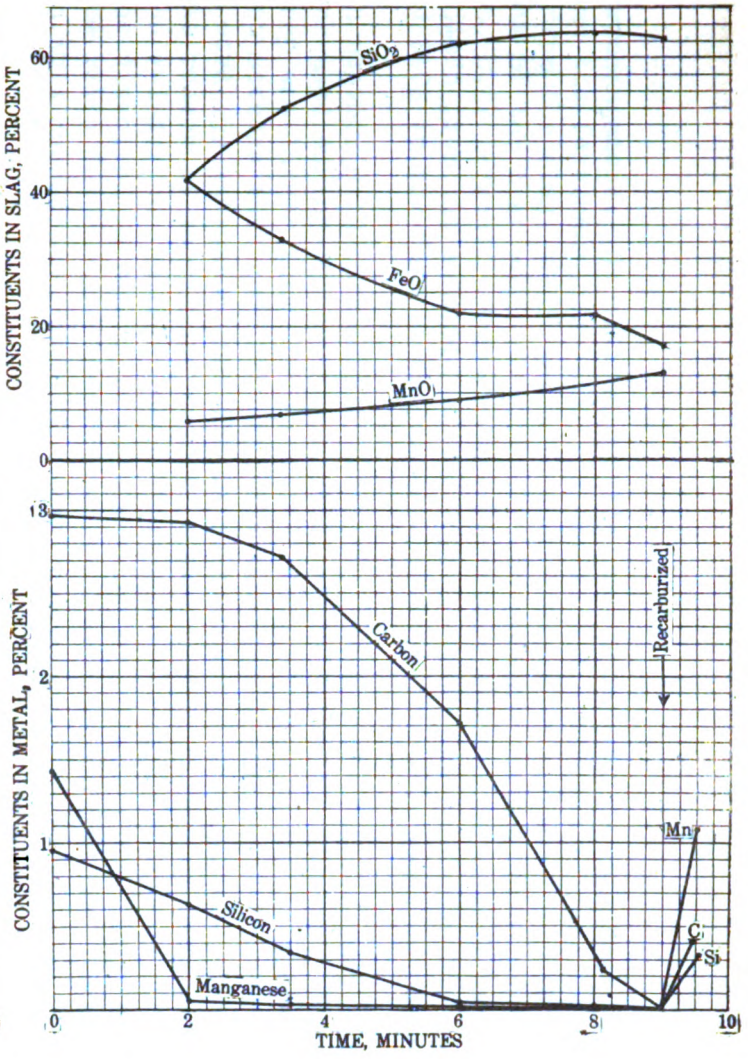

Figure 46.- Elimination of manganese, carbon, and silicon in acid bessemer process.

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the ferromanganese. No silicon addition was necessary in this heat because by the time the ferromanganese addition was made 0.3 percent silicon had been reduced from the slag, which was more than enough for deoxidation. The average analysis of the heat was: Manganese, 0.64 percent; carbon, 0.49 percent; and silicon, 0.27 percent. These values represent a decrease in both manganese and silicon from the analysis of the tapping test, due to elimination of some MnO and SiO_2 in the form of manganous silicates from the metal to the slag.

In another acid open-hearth heat (263) manganese, silicon, and sulphur all decreased during the pouring period, which lasted 20 minutes. The manganese drop was larger than the equivalent drop of sulphur and it was suggested by these authors that some MnO probably had formed along with the MnS. More recent work (9) indicated that MnS is quite soluble in manganese silicate, and for this reason it is highly possible that the elimination of manganese, silicon, and sulphur as indicated above took place through the medium of manganese sulphide dissolved in manganese silicate inclusion particles. Such particles would be quite fusible and should readily flux with one another. The elimination in this connection should be relatively rapid.

The heat shown in figure 51 represents one of the best practices in the acid open-hearth furnace because of the high manganese content of the slag which was carried throughout the heat. In many American steel plants the FeO content is higher than the MnO. Better results have been indicated by the former practice, which has as one of its benefits the carrying of a higher residual manganese throughout the heat. Such a process requires less deoxidation.

Manganese in Acid Bessemer Furnace

The American practice in the acid bessemer furnace involves elimination of the constituents manganese, silicon, and carbon by blowing air through a bath of liquid pig iron. The American practice differs from that used in other countries in that low-silicon pig iron is used to diminish the "blow" or refining time. Just enough silicon (0.8 to 1.2 percent) is used to give sufficient heat from the oxidation of silicon to insure that no solidification of the metal is experienced during the carbon-elimination period. Fairly low-manganese pig iron is used in the American practice, the average manganese analysis being 0.40 percent. The English, German, and Swedish practices are much slower than the American, inasmuch as the silicon content of the pig iron is approximately 2.00 percent and the manganese also is somewhat higher — 0.90 percent. Occasionally even much higher manganese and silicon contents than these are used in foreign practice. Regardless of the percentage of the constituents of the pig iron in all of the recorded acid bessemer heats, elimination of manganese preceded elimination of silicon. In every instance the manganese was virtually eliminated before the silicon was half removed. This is probably due to the acid lining, inasmuch as the formation of SiO_2 would be inhibited by the SiO_2 lining. Also, oxidation of the manganese probably is rapid in this case, because of the secondary reaction which involves the formation of a manganous silicate.

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In Germany still another practice is popular. The temperature of a metal bath is allowed to increase until the carbon is eliminated in preference to the manganese and silicon. In this manner a low-carbon steel containing appreciable amounts of residual silicon and manganese is made. The reason for this practice is that it is much easier to obtain a desired specification, and further recarburization and deoxidation in the ladle are not required. In one instance to be found in the literature (361,p.106), at the end of the blow the carbon had been eliminated to 0.1 percent, the silicon to 0.34 percent, and the manganese to 0.60 percent by this type of procedure. No additions were made to the ladle because these values were within the desired specifications for the steel.

An example of the relative elimination of manganese with regard to the elimination of silicon and carbon is shown in figure 46. In this particular heat (361,p.106) a liquid pig iron was charged which contained: Carbon, 2.96 percent; manganese, 1.42 percent; and silicon, 0.94 percent.

Within 2 minutes after the blow was started, virtually all of the manganese had been eliminated, being reduced to approximately 0.1 percent. Virtually no carbon had been eliminated and only about 25 percent of the silicon, the latter being reduced to 0.62 percent. By this time a slag had formed that contained MnO and FeO from the oxidation of the iron and manganese by the air bubbling through the liquid steel. Also, these two oxides had eroded the converter lining to such an extent, and enough SiO_2 had been formed by oxidation, so that approximately 40 percent was present in the slag. During these first stages the FeO content of the slag was quite high, as shown, but soon was diluted by the above fluxing procedure until only 20 percent of FeO was present in the slag. By this time virtually all the silicon in the metal had been eliminated. The passage of more air through the vessel was required, however, to remove the remainder of the carbon. This was done within a 3-minute period between 6 and 9 minutes plotted on the figure. The MnO content of the slag remained fairly constant throughout the heat (6 to 8 percent) until tapping, when spiegeleisen was added to the ladle. At this point the MnO content of the slag increased to 13 percent. The analysis of the steel was affected as the diagram indicates. The spiegel addition to the ladle raised the contents not only of manganese but also of carbon and silicon. Virtually all of these constituents were very low at the time of the addition, and the final analysis was: Manganese, 1.15 percent; carbon, 0.45 percent; and silicon, 0.38 percent. As has been explained in the previous sections, spiegel is an alloy of iron, manganese, silicon, and carbon, each in sufficient proportions to affect the analysis as indicated.

Manganese in Basic Bessemer Process

Although no basic bessemer operations are being conducted in the United States at present, the process is interesting from the standpoint of manganese metallurgy when contrasted with the acid process so popular in this country.

Wedding (379) described a heat by Finkener at the Rhine Steel Works in 1883 which seems to typify other basic heats made and described since that time.

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As would be expected, the manganese is not eliminated as readily in this practice as in the acid furnace. (See fig. 47.) The silicon oxidizes first to SiO_2 and is then carried to the slag to become a constituent part of the calcium silicate. During this stage the manganese is eliminated slowly, and after 8 minutes of the blow holds fairly constant at 0.14 to 0.18 percent, while the carbon blow or elimination is taking place. When most of the carbon has been eliminated the manganese again oxidizes, as shown by the small value (0.01 percent) indicated after 15 minutes and 13 seconds of the blow. Subsequently only a trace of manganese remains.

The manganous oxide in the slag decreased (as indicated in fig. 47) after 5 minutes and 21 seconds of the blow, although some of the manganese in the metal was still being eliminated to the slag. This effect was probably due to the fact that the lime usually charged in the bottom of the furnace came to the slag surface after 5 minutes and took some time to dissolve all the lumps in the slag. During this process the manganous oxide was diluted, and its concentration decreased.

The chief reason for using the basic practice is to remove the phosphorus from high-phosphorus pig irons. This is accomplished by means of the afterblow. The liquid iron is allowed to cool some time after the silicon, manganese, and carbon have been eliminated. The secondary blow is then started, which involves the oxidation of the phosphorus to P_2O_5, followed by the formation of $3CaO \cdot P_2O_5$ in the slag. Some writers also contend that $(MnO)_x (P_2O_5)_y$ forms during this period. In this particular heat the afterblow was started at 15 minutes 13 seconds after charging and lasted until 19 minutes 49 seconds, during which the phosphorus content of the metal was decreased from 2.000 to 0.087 percent.

Some conception of the manner in which manganese reacts during the refining of steel in the basic bessemer process was obtained by Faust (90). This investigator obtained slag and metal samples from various heats in which the manganese content of the liquid pig iron charged was increased. A relation was established between the ratio of manganese to iron in the slag and the manganese content of the pig iron, and it was found that the ratio increased from 0.4 to 0.7 by increasing the manganese content of the pig from 0.6 to 1.8 percent.

It was also found that the amount of manganese oxidized in the basic bessemer remained fairly constant at 85 percent, although the manganese content of the refined metal increased from 0.15 to 0.25 percent by means of the same increase in the manganese content of the pig iron.

Another relation was established between the manganese content of the refined metal and the ratio of MnO to FeO in the furnace slag and is expressed as follows:

$$\text{Percent Mn in metal} = 0.4 \times \frac{\text{Percent MnO in slag}}{\text{Percent FeO in slag}}.$$

As shown above, the ratio of these constituents in the slag varies from 0.4

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to 0.7, and in accordance with this the manganese content of the metal would necessarily range from 0.16 to 0.28.

Manganese Reactions in Basic Electric-Arc Furnace

The most common melting practice in the basic electric furnace involves charging cold scrap to the furnace, melting down under an oxidizing slag, and removal of this first slag followed by preparation of a synthetic slag. The synthetic slag is prepared from lime, fluorspar, and coke and is usually identified by the term "carbide slag". The purpose of this secondary slag is to prevent oxidation by recarburization and stabilizing of the analysis of the metal so that time may be allowed for an analysis to be received from the laboratory. Variations in analyses for carbon, manganese, and silicon in a typical ball-bearing steel heat (349) are shown in figure 48. The manganese reactions in this heat are quite simple, as can be readily seen from the curve. Manganese in the scrap charged in the furnace was approximately 0.40 percent and during melting under the oxidizing slag was reduced to approximately 0.25 percent. Shortly after the melting down the first slag was raked off and a carbide slag put on, and a slight increase in the manganese content of the metal is noted. If the first slag had been entirely removed in this heat, it is quite doubtful if any increase at this time would have been indicated, inasmuch as there would not have been any source of manganese other than that already in the metal bath. At 9:15 clock time on the chart, ferromanganese was added to the heat, thereby increasing the manganese content to 0.35, at which concentration it remained for the remainder of the heat. Some increase in the carbon content was noted, which was probably due to both the carbon in the ferromanganese and that in the ferrochrome, which was also added at 9:15. At 9:50 wash metal was added to the bath to increase the carbon content of the metal without increasing the manganese. Wash metal, as it is known, is essentially an iron-carbon alloy and contains very small amounts of manganese and silicon. The effect of the ferrosilicon addition on the silicon content of the metal is indicated clearly on the chart. The slag analyses plotted in the upper portion of figure 48 indicated that there was little or no manganese in the carbide slag. The first or oxidizing slag contained approximately 5 percent MnO, but this was removed by slagging at 8.34. The manganese content of many low-alloy and plain-carbon tool steels is quite low compared with steels made by other processes. The ladle analysis of the heat just described indicated the presence of 0.34 percent manganese. Various other specifications for steels of this type require a final manganese analysis of 0.25 to 0.45 percent. As can be seen from the description of the above heat, the only attention given manganese in the electric furnace is a small addition of ferromanganese toward the latter part of the heat and under the carburizing slag. The loss of manganese under these conditions is slight.

The basic electric furnace is also used for preparation of high-manganese steels, such as the austenitic steels containing as much as 10 to 15 percent of this constituent. In the preparation of these materials in the basic electric furnace a somewhat higher residual manganese is carried throughout the heat, followed by large additions of sometimes both low- and

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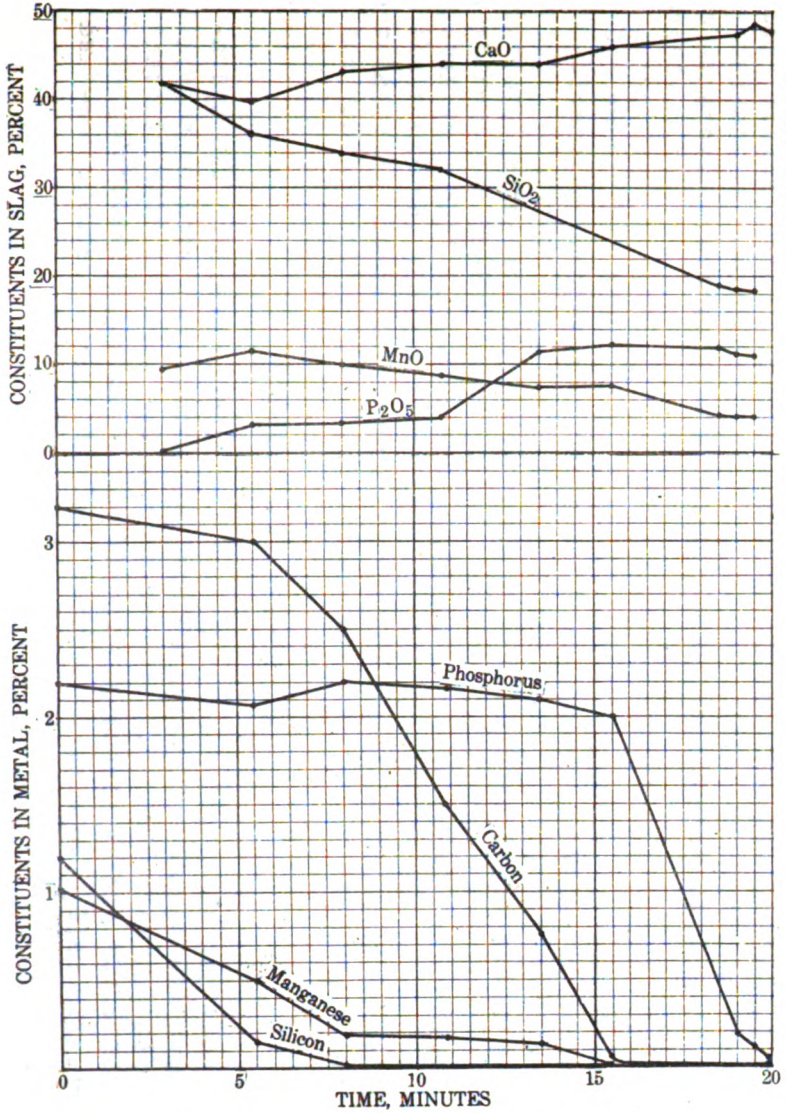

Figure 47.- Manganese reactions in basic bessemer process (Finkener).

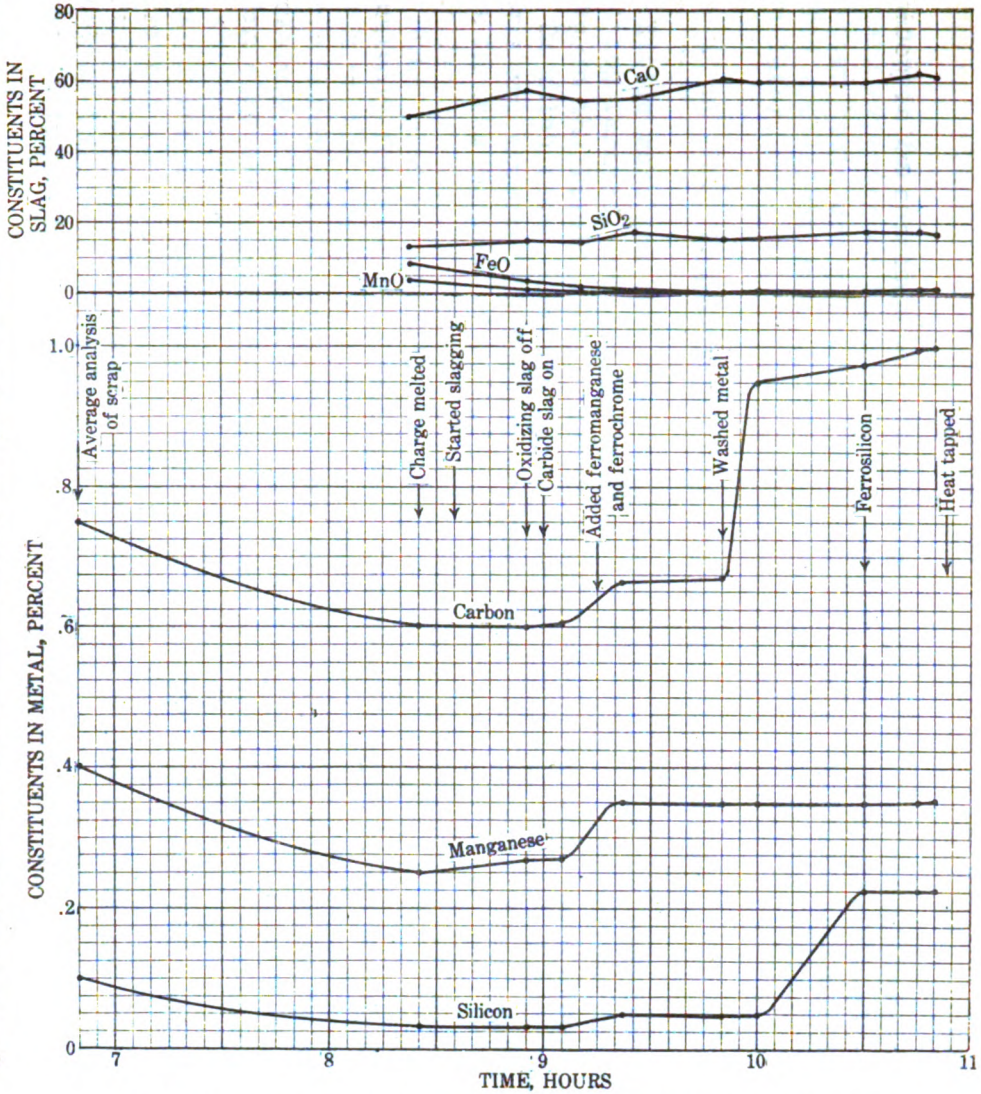

Figure 48.- Manganese reactions in basic electric arc furnace (Sisco).

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high-carbon ferromanganese. In this instance also only slight losses of manganese are experienced because of the carbide slag. If accurate analyses of melt-down tests are given to the melter he has no difficulty in meeting the desired specifications. A more complete description of these steels will be given later.

Manganese in Coreless Induction Furnace

Little work has been done toward refining steel in the high-frequency induction furnace, principally because of the vigorous convection currents set up in the liquid steel. Recent developments, however, have shown several ways in which these currents may be reduced considerably, and future investigations are expected to involve studies of various types of basic and acid slags for the purpose of refining steel in this type of furnace.

Under present conditions the high-frequency furnace is used almost exclusively for remelting processes. Oxidation reactions occur but are due largely to the atmosphere above the moving metal bath, and in many instances these are reduced by large additions of some deoxidizer, such as ferrosilicon, immediately after melting down. If no deoxidizer is added some of the oxide-forming elements already in the steel scrap are oxidized and eliminated to a slag which forms a rim at the top of the crucible. Because this rim of slag is out of the high-temperature zone it is usually solid and does not appreciably affect the reactions. The oxidation of steel by the atmosphere in this type of furnace has been studied (389) and the results may be briefly described as that in a basic-lined furnace (magnesite) oxidation of silicon from the scrap is much more rapid than oxidation of manganese. The opposite is true in the acid-lined furnace, inasmuch as the oxidation product SiO_2 is already present in the refractory lining. This of course holds back the silicon reaction. Similar differences in velocities of reactions have been noted in previous sections in which acid and basic open-hearth heats were compared.

One author has added as much as 2 percent manganese to such steel, but the CO blowholes persisted in the solidified material. This is also the experience of Körber (211). In fact, it has been pointed out (94) that the C–FeO reaction is slightly endothermic at steel-making temperatures (1,600° C.), whereas the Mn–FeO reaction is slightly exothermic. Some indications show that at 1,583° C. carbon and manganese may have equal tendencies to form their oxides, whereas above this temperature carbon reacts more strongly than manganese. Below this temperature the reverse is true, in accordance with the recommendation that high temperatures result in manganese savings.

Manganese in Wrought Iron

In the old puddling process for making wrought iron cold pig iron was usually charged into a reverberatory-type furnace. The charge was usually melted within half an hour, and as soon as possible iron oxide was added to remove the various metalloids of the liquid pig iron. Within 10 to 20 minutes the manganese content had been reduced 90 percent. With elimination

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of carbon, silicon, and manganese the melting point of the iron was raised, and solidification or "graining" began. The puddler soon started to separate the granulated material into several lumps, which he kneaded into small balls to squeeze out some of the slag formed through reaction of the above constituents with iron oxide. All these lumps of granulated metal were then worked together into one large lump and finally withdrawn from the furnace and sent through a rotary squeezer that removed a considerable portion of the remaining slag. The manganese remaining in the wrought iron thus formed (0.05 percent) is probably present as MnS, MnO, and some small amounts of the alloy manganese.

This procedure has recently been supplanted by the Aston (11) process, which essentially involves refining of liquid pig iron in the acid bessemer and pouring of this material into a ladle of synthetically prepared ferrous silicate slag. The manganese reactions involved are the same as those previously mentioned in the description of the acid bessemer process. It can be seen that virtually all the manganese in the original pig iron is eliminated.

Manganese Reactions in Liquid Steel

Because of the important economic situation with regard to manganese considerable research has been done with the hope of determining the various equilibria of manganese reactions in liquid steel. Many such attempts have been made without consideration of the complicated furnace slags.

Manganese — The Deoxidizer

Manganese has been overrated as a deoxidizer for steel. Many authors discuss the deoxidation of steel with manganese as though the reaction is quite strong, and no further deoxidation is necessary if manganese is added. The strength of a deoxidizer is reflected in its ability to inhibit the reaction between carbon and iron oxide. In other words, it should be a better deoxidizer than carbon. In this regard manganese is only slightly better than carbon.

In making low-carbon rimming steel, 0.20 to 0.30 percent manganese is added to the furnace and ladle in the form of ferromanganese or spiegel. No other deoxidizer is employed. When this material is poured into the molds enough carbon monoxide escapes to give the appearance of boiling. The solidified ingot has the well-known structure of rimmed steel, characterized by rows of blowholes equidistant from the ingot surface.

Giollitti (113) states that steel may be deoxidized to the point of inhibition of the C-FeO reaction by allowing enough time for the nearly colloidal product of the reaction MnO to rise from the steel bath into the slag. The manganese content must be maintained constant during this period, however, and sometimes several hours are required to produce thorough deoxidation. This idea has been consolidated in a recommended steel practice for the basic open hearth, which, as quoted from Giollitti, is as follows:

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> As soon as melting down is complete the bath should contain at least 0.60 percent carbon and 0.25 percent manganese. Only when these percentages are exceeded can small additions of ore be made with the view to shorten the first phase of the operation. Additions of ore must absolutely cease after the carbon has fallen below 0.55 percent and the manganese below 0.20 percent. When the carbon has reached 0.40 percent, successive additions of ferromanganese are made, adding each time about 0.25 percent manganese (referred to the total charge) so as to always maintain in the bath a percentage of manganese between 0.20 and 0.45 percent. In this manner the carbon is allowed to fall very gradually until it is brought down to 0.20 percent.

In one heat recorded, five additions of ferromanganese were made. This represents a costly but standard practice of a large European company in making high-grade steel.

Attempts have been made to determine the equilibrium in the reaction $FeO + Mn \rightleftarrows MnO + Fe$, in which manganese is dissolved in the liquid iron phase and the slag is composed of only FeO and MnO. These attempts have not been very successful, particularly because of refractory difficulties. A pure slag containing only these two oxides is very erosive on practically any type of acid or basic refractory material.

Other investigators have attempted to determine the effects of high concentrations of CaO and SiO_2 in the FeO-MnO slag phase. Many experimental difficulties have been experienced by this latter group of workers, as would be expected, inasmuch as analyses of open-hearth slags vary so widely. As was pointed out previously, an open-hearth slag is essentially a calcium silicate in which iron and manganese oxides are supposedly dissolved. In every investigation the assumption has been made that the reaction given above is homogeneous and that both FeO and MnO are at least slightly soluble in the slag and metal phases.

Calculations of Equilibrium for Reaction $FeO + Mn \rightleftarrows MnO + Fe$. - Probably the first investigation of this equilibrium was made by Le Chatelier (231). His work involved the calculation of the dissociation pressures of FeO and MnO from the Carnot-Clapeyron equation. The pressure values calculated by this author were:

$$p_{O_2}\ (FeO) = 10^{-8} \text{ atmospheres for reaction } 2FeO \rightleftarrows 2Fe + O_2,$$
$$p_{O_2}\ (MnO) = 10^{-14} \text{ atmospheres for reaction } 2MnO \rightleftarrows 2Mn + O_2.$$

Le Chatelier made these calculations by assuming that manganese and iron are completely miscible at steel-making temperatures and that the saturation concentration of FeO in liquid iron is 1.1 percent, and also that MnO is nearly insoluble in liquid iron. By combining the above two values,

$$K_{II} = \frac{p_{O_2}\ (FeO)}{(\text{per cent } FeO_{(sat.)})^2} = \frac{10^{-8}}{1.21}$$

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and $K_{III} = [p_{O_2}\ (MnO)]\ [\text{percent Mn}_{(sat. = 100)}]^2 = 10^{-14} \times 10^4$,

and $\frac{K_{III}}{K_{II}} = 0.0121$ for a bimolal reaction,

and K_I = equilibrium constant for the product Mn x FeO = 0.0121 = 0.11.

Styri (364) and McCance (249) calculated this constant in an identical manner, but used different values for the percent saturation of ferrous oxide in iron and for the dissociation pressures of the two oxides as calculated from the Nernst heat theorem. Their values are respectively 0.126 and 0.111. These investigators assumed throughout that manganous oxide was nearly insoluble in iron at 1,600° C.

Oberhoffer and Schenck (279) were not satisfied with these calculations and proceeded to make some experimental determinations. These workers pointed out the probability of manganous oxide having an appreciable solubility in iron and wrote their mass-action equation as follows:

$$K_1\left(\begin{matrix}\text{all materials}\\ \text{dissolved in iron}\end{matrix}\right) = \frac{FeO \times Mn}{MnO}$$

instead of the usual (Mn x FeO = k) expression.

Also, they considered the function of the liquid-slag phase above the liquid metal as representing a system of two immiscible liquids in and between which the MnO and the FeO were dissolved and distributed according to the Nernst distribution law.

In other words

$$L_1 = L_{FeO} = \frac{FeO_{(slag)}}{FeO_{(metal)}} \quad \text{and} \quad L_{MnO} = \frac{MnO_{(slag)}}{MnO_{(metal)}} = L_2$$

where L_{FeO} and L_{MnO} are the distribution coefficients.

Then with these ratios in mind they constructed a constant as follows:

$$1 \Big/ K_2 = K_1 \times \frac{L_{(FeO)}}{L_{(MnO)}} = \frac{FeO_{(slag)}\ Mn_{(metal)}}{MnO_{(slag)}}.$$

They then determined the value of K_2 to be $2.66 = \frac{(MnO)_{slag}}{(FeO)_{slag} \times (Mn)_{metal}}$.

No attempt was made by these investigators to determine the variation of K_2 with the temperature, and no values were obtained for the relation between MnO and FeO in the metal and their variation with the manganese content. Also the percentage of manganese (metal) as given by them is composed of both free manganese and manganese as MnO (or MnS), and the constant is probably smaller because of this correction.

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Benedicks and Löfquist (22) combined the work of previous investigators and calculated the variation of total oxygen with the manganese content of the iron by assuming that all combinations exist in the system iron-oxygen-manganese.

An attempt (95) has been made to calculate the equilibrium constant for the Mn-FeO reaction from available data, such as specific heats, heats of formation, fusion, etc. More reliable data are available now, and a recalculation should be made. The free energy was calculated for the reaction

$$FeO_{(s)} + Mn_{(s)} = MnO_{(s)} + Fe_{(s)} = -34,040 \text{ calories}$$

or

$$K = 9550 = \frac{MnO_{(s)} \times Fe}{FeO_{(s)} \times Mn} .$$

If FeO and MnO are both soluble in liquid iron, as assumed by Fitterer, the equilibrium constant should be modified accordingly.

The following constant was constructed:

$$K = \frac{\dfrac{\text{Percent } MnO_{(e)}}{\text{Percent } MnO_{(s)}} \times \text{percent Fe}}{\dfrac{\text{Percent } FeO_{(e)}}{\text{Percent } FeO_{(s)}} \times \text{percent } Mn_{(f)}} ,$$

in which the subscripts e and s denote "equilibrium" and "saturated" respectively; $Mn_{(f)}$ is the uncombined manganese in the iron determined by subtracting the manganese present as MnO from the total manganese. The MnO content of the iron was determined by the electrolytic method (95).

At 1,600° C. this constant was found to be 512. The saturation of MnO in the iron was found to be 0.333 percent, whereas the saturation of FeO at the same temperature (155) is 1.25 percent.

Some of the experimental work used in the determination of this constant was admittedly in error; but the electrolytic method offers a new solution to this problem, and it is hoped that future work will continue in this direction. It is particularly important to accurately determine the solubilities of MnO in iron at various temperatures. Unless this is done further consideration of this reaction must be postponed.

The most recent work on this reaction by Körber (211) involved the study of constant $K = \frac{MnO \times Fe}{FeO \times Mn}$, in which the oxides are in the slag phase. The constant was shown to range with temperature from 60 at 1,950° C. to 260 at 1,530° C. or the melting point of iron. Corrections were made for the solubility of FeO in iron but it was assumed that MnO was nearly insoluble, and

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no correction was made in this regard. It is to be regretted that no determinations were made of the MnO content of the metal. The samples prepared were of such a nature that this very important factor could have been determined once for all.

In this work, as in the others discussed above, no mention was made of the effect of complex open-hearth slags upon the equilibrium constant. The only practical instance in which these constants would apply occurs during the deoxidation of steel with a manganese alloy. If the saturation of MnO is exceeded, MnO particles thereof will be distributed throughout the bath. FeO is entirely miscible in MnO and FeO-MnO particles of these oxides would soon be formed. The metal surrounding these particles would then tend to approach equilibrium with the FeO-MnO slag.

In nearly all other practical cases the metal in which manganese, FeO, and possibly MnO are dissolved approaches equilibrium with a slag in which FeO and MnO are only minor constituents. The effects of the various slags on the equilibrium have long been a matter of speculation.

Characteristics of Manganese Deoxidation Determined from Open-Hearth Data -- Effect of Basic Slags. - Feild (92) calculated the constant $m = \frac{MnO}{FeO \times Mn}$ to be about 0.01 from metal analyses of a certain open-hearth heat. His MnO values were determined by calculating the decrease in FeO caused by known additions of manganese. This procedure does not indicate that equilibrium was established and must therefore be discounted. Likewise, no indication of the change of m with temperature was given.

Colclough (55) lists 10 values for this constant without temperature consideration and obtains an average value of about 1×10^3. Colclough, however, made one statement which expresses an observation made above -- namely, that no addition of manganese alone will completely inhibit the evolution of CO gas formed from the reaction of carbon with FeO.

Herty (150) combined the various relations previously determined by Keats and himself (195) in such a manner that a very useful equilibrium constant and its change with temperature were obtained. Certain corrections were necessary, and a later publication (156) by the same author discusses the constant as it stands at present.

The relationship selected by this investigator was the reciprocal of Oberhoffer's expression (equation A, p. 276) and is expressed as follows:

$$K' = \frac{(MnO)_{slag}}{(FeO)_{slag} \times (Mn)_{metal}},$$

wherein $(MnO)_{slag}$ and $(FeO)_{slag}$ are expressed in mole fractions and $(Mn)_{metal}$ is expressed as weight percent.

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The amounts of MnO and FeO in the metal phase were assumed to be proportional to those of the slag phase, according to the two distribution coefficients (L_1 and L_2) which were introduced by Oberhoffer.

Also, it was assumed that the MnO and FeO in the slag were probably associated in some manner with the acid constituents SiO_2 and P_2O_5, which are also present.

The extent of this association was likewise assumed to depend primarily upon the over-all balance of the following reactions:

$$\begin{aligned} 2MnO + SiO_2 &\rightleftarrows 2MnO\cdot SiO_2, \\ 2FeO + SiO_2 &\rightleftarrows 2FeO\cdot SiO_2, \\ CaO + SiO_2 &\rightleftarrows CaO\cdot SiO_2, \\ 3CaO + P_2O_5 &\rightleftarrows 3CaO\cdot P_2O_5. \end{aligned}$$

From the heats of formation it was assumed that the calcium silicate was probably the most stable compound and that the amounts of free MnO and free FeO were indirectly proportional to the amount of the free or the available base CaO. For these reasons, a correction factor (mole faction AB) 0.5 was applied to K' and the present constant being used for open-hearth calculations is:

$$K'' = \frac{(N_{MnO})_{slag}\,(N_{A.B.})0.5_{slag}}{(N_{FeO})_{slag}\,(\text{percent Mn})_{metal}}$$

where N = mole fraction.

The variation of this corrected constant with temperature was determined by means of Van't Hoff's isochore by assuming that the heat of reaction is constant in the temperature range considered. The expression developed was:

$$\log_{10} K_{Mn} = \left(\frac{10^5}{T} - 52.1\right) \frac{1}{8.88}.$$

Later the opinion was expressed that if the mole fraction of available base in the open-hearth slag is less than 0.3 the following expression can be used:

$$\log_{10} K_{Mn} = \left(\frac{10^5}{T} - 50.27\right) \frac{1}{6.27}.$$

In general, this expression seems to apply to open-hearth practice, particularly at such times when the rate of elimination of manganese is low, or, in other words, when the reactants are approaching stable conditions.

Schenck (337) made many calculations similar to Herty's on the available base concept. The various compounds such as the calcium silicates and their influence were assumed from various angles but in general brought this very complex problem no nearer satisfactory solution.

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Manganese Oxide in Steel. - As stated in the discussion of manganese reactions, some metallurgists believe that MnO resulting from the Mn-FeO reaction is entirely insoluble in steel. Others hold that inasmuch as the deoxidation reaction is reversible this oxide must be at least slightly soluble in liquid iron, otherwise the reaction would go to completion, and no manganese would remain in the steel.

Fitterer (94) melted electrolytic iron under MnO and held the melt at 1,600° C. The slag of course changed to an FeO-MnO mixture, but the metal was later found to contain 0.06 percent MnO by annealing and electrolytic extraction. This test indicates that MnO may be partly soluble in liquid iron, which is in equilibrium with an FeO-MnO slag. If enough manganese is added to steel so that the solubility of MnO is exceeded, MnO particles will be precipitated. These particles will also absorb some FeO from the surrounding steel.

Daniloff (62) found that FeO and MnO are miscible in all proportions, and the liquidus and solidus of the system FeO-MnO are regular curves leading from 1,360° C. at the melting point of pure FeO to 1,600° C., the melting point of pure MnO. This work has since been checked by Andrew (9). Precipitated MnO particles would then assume compositions designated by this diagram for temperatures within the above range.

Pure MnO crystals have been found (94) in iron to which 2 percent manganese had been added. These are reproduced in figure 49. Dendrites of MnO have also been found in the same samples as shown in this figure. Similar materials were found in steels deoxidized with 1.76 percent manganese by Körber (211).

MnO inclusions resulting from lesser additions of manganese sometimes are homogeneous solid solutions of FeO and MnO. Occasionally, however, they have the appearance illustrated in figure 50. It is believed that this type of particle rapidly passed through the region of solid-liquid immiscibility in the FeO-MnO system, and time was not allowed for homogenization. Otherwise, a homogeneous particle would have been observed. This structure appears in the large FeO-MnO inclusions and seldom in the smaller particles.

The particles of MnO or MnO-FeO described above assist greatly in removing more insoluble and refractory materials, such as SiO_2, from liquid steel. For example, low-melting particles of manganous silicates are formed when manganese-silicon alloys (152) varying from 4:1 to 8:1 in ratio of manganese to silicon are added to an oxidized liquid steel. These particles are fusible enough to coalesce whenever they come in contact.

It has been suggested that the mechanism of this action involves the formation of insoluble SiO_2 particles and soluble MnO (and possibly some MnO particles). MnO is absorbed into the SiO_2 particle so as to approach a slag-metal equilibrium, the slag in this case being numerous heterogeneously dispersed particles. As the manganese silicate particles are formed they rise toward the furnace slag surface, coalescing with each other until the majority have been eliminated from the metal bath. This requires a very

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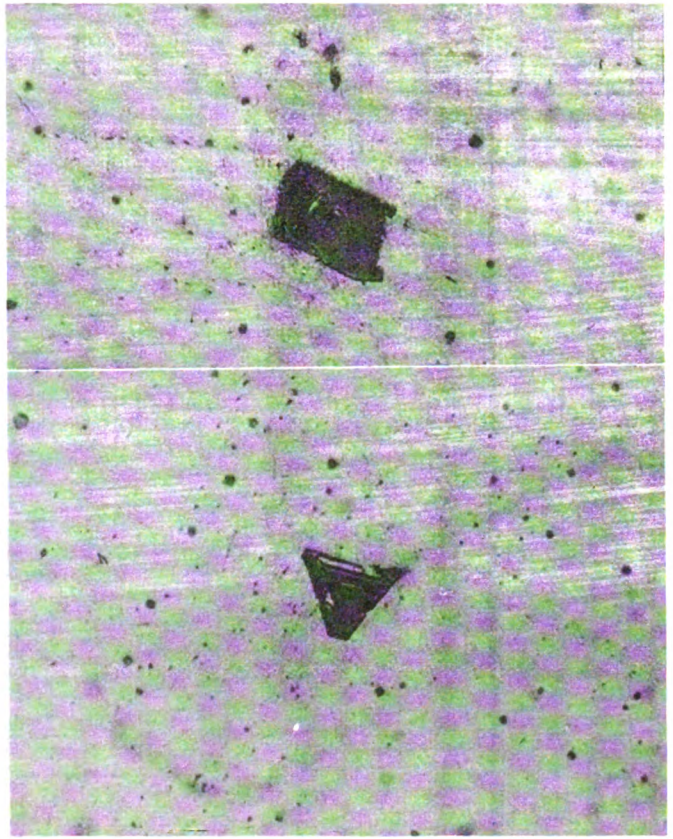

Figure 49.- MnO crystals in steel deoxidized with manganese.

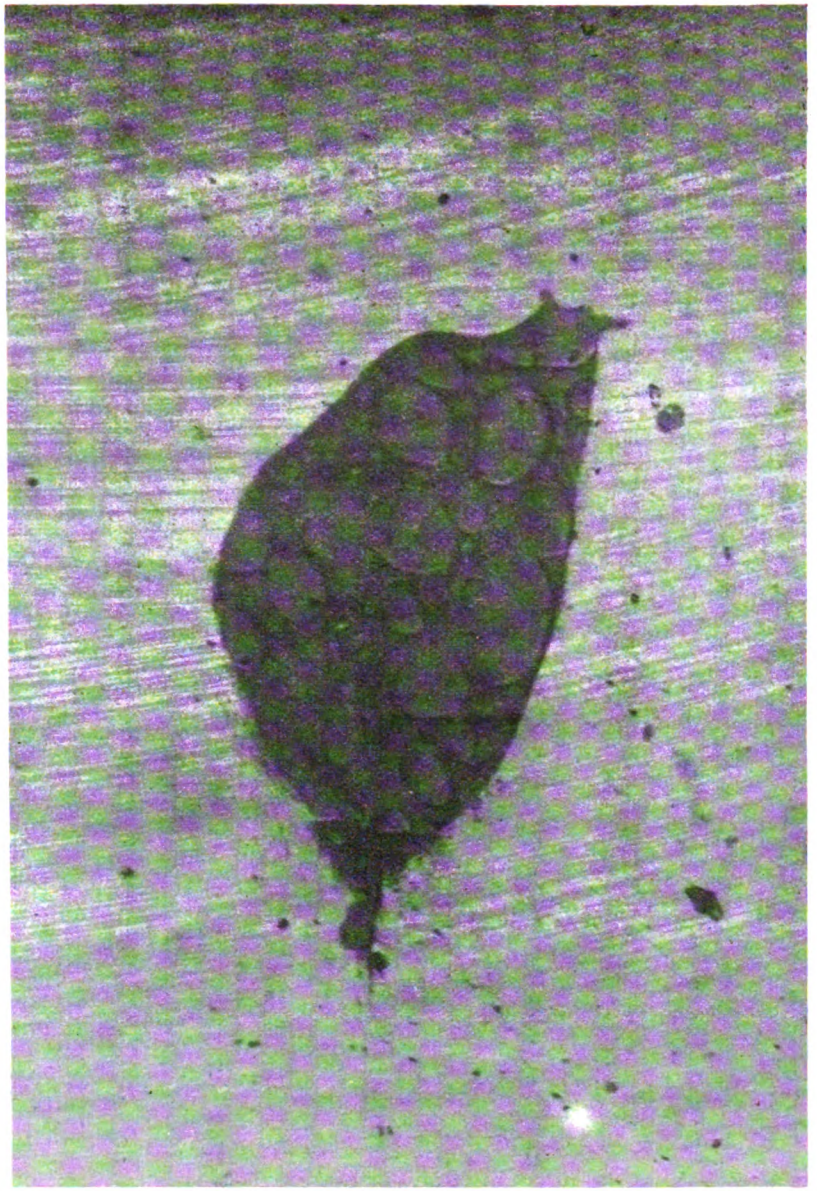

Figure 50.- FeO-MnO inclusion in steel partly deoxidized with manganese.

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short time, and the steel is left in the furnace only 5 to 10 minutes after the alloy addition.

This fluxing action of MnO is probably the basic reason for preparation of high-quality steel as suggested by Giollitti (113). The manganese-silicon alloys are probably more economical than this practice, however, and much less time is required for the "cleansing" action. This process has been discussed in detail on page 238.

Manganese -- Desulphurizer

As stated in the introduction to this section, the desulphurizing action of manganese in steel was predicted by the chemist Henderson (106) during the application of ferromanganese to English steels.

Soon after, Hackney (133) suggested that four times as much manganese should be added to steel as there is sulphur present; otherwise, difficulty would be encountered in rolling or forging the product. Stead (354) determined that the ratio of manganese to sulphur should be at least 8:1 to obtain the best beneficial effects of manganese.

MnS is less soluble in liquid iron and more soluble in slag than is FeS, and if given time some of these particles will rise and enter the slag phase, resulting in elimination of sulphur. According to McCance (250) 1 percent of manganese in pig iron will reduce the sulphur content 45 percent during the period between the tapping of the blast furnace and pouring from the mixer. An increase to 1.2 percent manganese will reduce the sulphur content 50 percent.

In later tests by Wheaton (402, pp. 1112-1114) the manganese was raised to as much as 2 percent, and the sulphur content of the pig iron was reduced almost 60 percent. Liquid pig iron has been held for considerable periods of time (153), and calculations were made of the residual manganese and sulphur remaining in the iron after virtually all of the manganese sulphide which had formed had been eliminated from the metal bath. A desulphurizing constant was calculated from these tests and was found to be:

$$K = (\text{percent manganese})\ (\text{percent residual sulphur}) = 0.070$$

at approximately 1,315° C. A similar relation calculated from Wheaton's data ranged from 0.057 to 0.066.

Many attempts have been made to calculate the equilibrium constant for the reaction

$$FeS + Mn = MnS + Fe,$$

but in most cases little important advancement has been made. The chief difficulty in this connection has been the difficulty in determining the quantities of FeS and MnS existing together in the steel under equilibrium

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conditions. Until recently the total sulphur could of course be determined, but the quantities of FeS and MnS could not be differentiated. The electrolytic extraction method offers a possible means for the solution of this problem.

In the basic open-hearth process various reactions may take place which involve sulphur elimination. The Mn-FeS reaction is probably the determining process in the metal bath, but when the MnS particles rise to the slag surface other reactions (principally that between CaO and MnS) occur.

The influence of the basic open-hearth slag and gas phases upon sulphur elimination was studied by Köhler (209). In general, he found that if the basicity of the slag as expressed by $\frac{CaO - 4P_2O_5}{SiO_2}$ ranges from 2 to 3 the ratio of sulphur in the slag to sulphur in the metal is more than doubled for the same manganese content. For example, with a basicity of 2 and a manganese content of 0.15 percent, the distribution ratio of sulphur between slag and metal is 4.5. If the basicity is raised to 3 at the same manganese content of the steel the distribution ratio is raised to 7. This effect has been explained in two ways:

1. Increased basicity means an increase in the CaO content, hence the reaction CaO + MnS (or FeS) = CaS + MnO (or FeO).

2. An increase in CaO-content of the slag desulphurizes the steel by the following two reactions:

$$CaO + MnO \cdot SiO_2 = CaO \cdot SiO_2 + MnO$$
$$MnO + FeS = MnS + FeO.$$

Manganese Sulphide in Steel. - According to Rohl (318), MnS and FeS form a simple eutectic system with the eutectic at about 6 percent MnS. The melting point of FeS is given at about 1,180° C., whereas MnS is shown to melt at 1,620° C. The eutectic temperature is slightly lower than the FeS fusion temperature. At the melting point of iron 25 percent FeS is soluble in MnS, and precipitated MnS particles could absorb up to this quantity of the iron sulphide. If sulphide inclusions are ever found in steels uncontaminated with oxides, particularly the silicates, they probably are composed of mixtures of the two. FeS precipitated on cooling from the freezing point of iron could of course be present.

Arnold and Waterhouse (10) determined that steel which was red-short, or cracked and broke on rolling or forging, contained FeS. Microscopic study of this impurity revealed that it was probably soluble in liquid iron but was precipitated in the grain boundaries as envelopes. Additions of manganese gradually changed the appearance of these envelopes to small rounded particles, presumably composed largely of MnS. This concept of the beneficial action of manganese is generally accepted.

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Conservation of Manganese in Steel-Making Processes

It has already been pointed out in this section that considerable portions of the manganese introduced into the various steel-making processes are lost. Possibly one of the greatest losses is reported in the basic bessemer process, in which up to 85 percent of this metal is removed by oxidation into the slag phase. Somewhat smaller proportions are dissipated in the other processes, but the losses are always large. Some of the ways in which these losses can be reduced are listed in the following pages.

Use of Liquid Ferro-Alloys

Many suggestions have been made concerning the use of liquid ferromanganese for steel and its advantages over that in which cold alloys are added. It was employed in European plants for many years before it was introduced into this country, the general practice being to melt the alloy in the arc electric furnace and to add the liquid material to the open hearth or bessemer ladle at the time the heat is tapped. Some advantages which have been recorded follow (175):

1. 5 to 30 percent ferromanganese is saved, inasmuch as the liquid alloy is added to the tapping stream and does not come in contact with the slag phase. In the ordinary practice in which the cold alloy is added to the liquid steel in the furnace fairly large lumps must be added some 20 minutes before the heat is tapped, and these lumps are in contact with the slag and therefore are oxidized by that medium before dissolving into the metal phase.

2. The time required to process the steel, particularly in the open-hearth furnace, is shortened because the 20-minute period listed in item 1 is eliminated. If time is not allowed for the cold alloy to dissolve in the metal bath and diffuse throughout, a homogeneous steel will not be obtained.

3. The manganese content of the finished steel is far more uniform with liquid-alloy additions than with solid material.

4. It is unnecessary to raise the temperature of the metal bath before the alloy addition, as is necessary with the addition of cold material. In the manufacture of a number of steels it is advantageous to keep the tapping temperature of the heat as low as possible, and the addition of the liquid alloy is very helpful in this respect.

5. Another advantage in the use of the liquid alloy is that alloy lumps of any size may be used. When cold alloy is added to the furnace it is necessary for the material to be in large lumps so that enough of each lump is well beneath the slag and in the liquid metal so that it will dissolve without great loss. If fine particles of ferromanganese were added the efficiency of the addition would be very low because of

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reaction with the slag phase. In the liquid process, however, particles of any size may be premelted in the electric furnace without loss.

6. Sometimes rephosphorization of the metal occurs through reaction of solid ferromanganese with the slag phase, involving deoxidation of the P_2O_5 present in the slag. In the liquid process the alloy does not come in contact with the slag, and because of this no rephosphorization has been observed.

The economy of liquid ferro-alloy additions has been criticized by various investigators, who state that the power requirements for melting ferromanganese or spiegel in the electric furnace are too large to make the process feasible. An itemized list of costs in this practice has been given by Hummel and is found to be approximately $25 per ton of ferromanganese, of which the power is approximately two-fifths. These figures were obtained on all types of electric furnaces in which the amount of power required per ton of ferromanganese was approximately 700 to 900 kw. h., and in addition to this 80 kilowatts were required per hour for holding the material liquid in the furnace. Unquestionably, these power requirements have since been decreased considerably because of more efficient furnaces, and it is believed that the melting requirement is closer to 500 kw. h. at present. In addition, the price of power per kilowatt-hour has been decreased in this country in the past few years. Other factors that counterbalance the cost of making liquid ferromanganese additions are: (1) the time saved in melting, dissolving, and homogenizing the manganese alloy in the liquid steel; and (2) a decrease in the manganese losses through the elimination of slag reactions.

High Melting, Refining, and Tapping Temperatures

Killing (203) has pointed out that the maintenance of high temperatures throughout the various steel-making processes will increase the amount of residual manganese obtained at the end of the heat. In other words, it is believed that because oxidation of manganese in steel-making processes is exothermic the tendency for oxidation would decrease with increasing temperature. This contention accords with the work of Körber (211) and others on the study of the equilibrium of the reaction $FeO + Mn = MnO + Fe$. The manganese constant given by this author ranges from 260 at 1,530° C. to approximately 100 at 1,800° C., showing that the tendency for MnO to form decreases through this temperature range.

One of the authors knows two open-hearth melters in the same plant; one consistently operates his furnaces at a higher temperature than the other. It has been observed that this melter also has higher residual manganese in his steel before tapping than does the other, although the material charged in each instance is about the same. This fact seems to bear out the contention that high temperatures result in saving of manganese.

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Use of Spiegel in Place of Ferromanganese Additions

After the World War, when manganese economy became a major issue of the steel industry, many observations were made concerning the substitution of spiegel for ferromanganese in the manufacture of many different types of steel. Most of those who discussed this point admitted that ferromanganese was necessary for certain grades of steel, but it was also their contention that in the majority of instances spiegel is a very worthy substitute. For example, Hibbard (162) pointed out that spiegel could be used instead of ferromanganese for 70 percent of the steel made in this country. The advantages of ferromanganese listed by that author were: (1) The quantity of material which must be handled is smaller; (2) if ferromanganese is added to the ladle preheating or premelting is unnecessary; (3) the material may be easily broken to any desired size; and (4) ferromanganese has a high ratio of manganese to carbon (approximately 12 to 1) and is therefore useful in making low-carbon steels.

Contrasted with these are various advantages in the use of spiegel. The manganese losses in spiegel additions are lower than in ferromanganese additions, probably because of the function of silicon in the spiegel as a deoxidizer. A spiegel mixture can be used to advantage for recarburization in the open hearth. A liquid mixture composed of spiegel, pig iron, and ferrosilicon may be added to the ladle in such plants where recarburization practice is followed. It has been found that by varying the amounts of these materials in the mixture virtually any analysis for carbon, manganese, and silicon may be obtained. Also, there is no need to add any other deoxidizer, inasmuch as enough silicon is added through the medium of this mixture. When only spiegel is added, it is feasible to charge three fourths of the total amount in the furnace and one fourth in the ladle for high-carbon steels. In low-carbon steels the addition may be divided into halves for furnace and ladle additions.

In answer to a questionnaire distributed by the Iron Age (57) to 70 steel companies in the United States it was found that spiegel is just as satisfactory as ferromanganese for high-carbon steels. During the late war these companies found it necessary to make spiegel additions when ferromanganese was not available or where the price of ferromanganese prohibited its use. Many of these companies are continuing this practice for some types of steel. In the companies questioned, 25 to 75 percent of the ferromanganese additions had been replaced by spiegel. High-manganese pig iron (2 to 3 percent manganese) was also considered in this questionnaire, and it was found to be an advantage by those companies who used it.

Use of high-silicon spiegel. - The substitution of spiegel for ferromanganese was again suggested by Herty (149), who recommended that not only ordinary spiegel could be used for this purpose but also silicospiegels could be used with secondary advantage. This material (152), which varies in manganese-silicon ratio from 4:1 to 8:1, has been found to be a very good deoxidizer of steel, not only because it inhibits the C-FeO reaction but also the products of deoxidation combine to form manganese silicates which, because

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of their fusibility and coalescence, are rapidly eliminated from the steel bath. Through the use of this material, at least in the basic open-hearth furnace, the amount of ferromanganese required in conjunction with this type of deoxidizer is 15 to 88 percent less than that required in regular practice. Also, these manganese-silicon alloys are being prepared from some of the domestic manganese ores, and if generally used the import requirements of this country for high-grade manganiferous ores could be greatly reduced, with accompanying increase in steel quality.

In many American steel companies a standard practice is to reboil the steel with ferrosilicon or silicon pig. The object of this procedure is to hold the steel in the deoxidized condition long enough for a carbon analysis to be reported on the heat before tapping. The steel composition may then be adjusted to meet desired specifications. Considerable information was obtained in connection with this practice at the United States Bureau of Mines (159), and it was found in general that the iron oxide content was essentially the same after reboiling as it was before the silicon addition. In many plant contacts made during this work it was found, however, that the opinion of the practical man was that this not only deoxidized the steel but also removed oxide impurities other than FeO, which were present before deoxidation. In other words, the addition "cleansed" the metal. That this is not true may be seen by reviewing the work mentioned above.

For an alloy to deoxidize steel and at the same time eliminate the deoxidation products, the resultant oxides must form large inclusion particles very soon after the alloy addition. If such large particles are formed they will be eliminated according to Stokes' (317) law or at a rate dependent upon the difference between the density of the oxide particles and the density of the iron and upon their particle size. The particle size is by far the more important factor, inasmuch as Stokes' equation involves the square of the radius. Hence, if an alloy produces large particles immediately after its addition, these globules will be more rapidly eliminated to the slag than will the iron oxide in the slag diffuse back into the metal bath. If the heat were tapped at this time the steel would not only be thoroughly deoxidized (free of FeO) but also would contain little or no oxides resulting from deoxidation reactions.

Manganese-silicon alloys will produce these results, as has been shown previously. The average size of a silica particle resulting from the deoxidation of steel with silicon is approximately $15 \cdot x10^{-4}$ centimeters. The average size of particles formed through deoxidation with manganese-silicon alloys of the above mentioned ratios of manganese to silicon is approximately $900 \cdot x10^{-4}$ centimeters. If the average radii of these particles were squared and placed in the equation for Stokes' law it would be found that the manganese silicate particle would rise to the slag surface 3,600 times as fast as the pure silica particle. The time required for elimination of the various size particles from liquid steel has been calculated by means of Stokes' law and is shown in table 86:

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TABLE 86. - Rate of Rise of Manganese Silicate Particles in Liquid Steel

Size of inclusion, cm. x 10^{-4}	Maximum rising velocity, inches/minute	Least time required to rise through, minutes	
		30-inch open-hearth bath	12-foot ladle
5	0.061	493.00	2360.00
10	.245	122.00	587.00
50	6.120	4.93	23.60
100	24.450	1.22	5.87
500	612.000	.05	.24

The time required for a given size particle to rise through a 30-inch open-hearth bath (as in a 100-ton open hearth) and also in a 12-foot ladle has been calculated. An inclusion whose diameter is above 100×10^{-4} centimeters would rise from the bottom to the top of a 100-ton open-hearth bath in approximately 1.25 minutes, providing that convection currents in the bath would not force it downward. Under these circumstances any particle above this size would probably be eliminated before samples of the steel could be taken after the alloy addition. That this is true has been proved from practical experience. Manganese-silicon alloys deoxidize steel very rapidly, and very few inclusions of any kind have been found in samples taken 2 or 3 minutes after the alloy addition. Also the steel contains negligible amounts of iron oxide.

Mechanism of deoxidation of steel with manganese-silicon alloys. - The densities of manganese-silicon alloys are somewhat less than those of the liquid steels. Hence, when the alloy is added to the metal bath a portion remains above the surface of the metal. This portion is in contact with the furnace slag, reacting with some of the oxides, particularly the iron oxides. Hence the alloy is added in fairly large lumps to have as much contact as possible with the metal phase, this resulting in greater efficiency of the alloy and its rapid solution in the bath.

Soon after the alloy has gone into solution the manganese and silicon react with iron oxide to form their respective oxides (MnO and SiO_2). The amount of these materials formed depends upon the amount of FeO present in the bath at the time of the addition and the amount of the two deoxidizers added, and also upon the relative rates of the reactions and their equilibrium constants. Both silicon and manganese will tend to establish an equilibrium depending upon these constants, and the balance between the reactants FeO, Mn, and Si and the resultant products MnO and SiO_2 is the relation that determines the formation of large manganese silicate particles. The mechanism of formation of the manganese silicates is dependent upon the slag system MnO-SiO_2. It is believed that silica is only slightly soluble in liquid iron, and by far the largest portion of this material will be precipitated as globular particles, whereas manganese oxide has an appreciable solubility in liquid iron. The silica particles would then be in

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contact with iron, which is saturated with manganous oxide. At steel-making temperatures silica is saturated with manganous oxide when the resultant silicate contains 40 to 50 percent MnO (158), hence there the MnO tends to be distributed between the liquid iron and the solid silica particles, and it is believed that this distribution is the mechanism which forms large manganese silicate particles. The electrolytic analyses of rapidly solidified steels which had been deoxidized with manganese-silicon alloys indicated that the inclusion particles are usually composed of equal portions of MnO and SiO_2.

A silicate of this composition has a relatively low fusion temperature, and if any of these particles come in contact with each other it is apparent that they will probably coalesce to form larger ones. Coalescence is a function of probability of contact, convection currents, and surface tension. The surface tension of these particles has been shown previously to be an important property.

Because of their low densities the manganous silicates should and do rise through the metal bath to the slag surface and eventually become a constituent part of the slag. That this mechanism is quite rapid has been already discussed when it was stated that samples taken soon after addition of the alloy were relatively free from both iron oxide and silicate particles, showing not only that the metal has been deoxidized but also that the manganous silicates have been eliminated to the slag phase.

Application of manganese-silicon alloys to steel manufacture. - The amounts of high-silicon spiegels to be added to any steel bath are limited by the following factors: (1) The analysis of the alloy; (2) the specifications of the finished steel; and (3) the minimum amount which can be added and still deoxidize the heat. It is apparent that the amount of alloy added should be kept lower than the manganese specification on the heat. The silicon specification is not so important, inasmuch as only relatively small portions of this element are added through this medium. The carbon analysis is an important factor in the use of this alloy in low-carbon steels but plays a minor role in the manufacture of the higher-carbon steels (above 0.40 percent).

In general, it has been the practice to use a silicospiegel containing approximately 20 percent manganese, 4 to 5 percent silicon, and 4 to 6 percent carbon in the manufacture of high-carbon steels. The silicomanganese alloys, however, are more useful when low-carbon killed steels (0.15 percent) are being prepared. In this case an alloy containing 70 percent manganese, 13 percent silicon, and 2 percent carbon has been used successfully without causing difficulty in meeting the specifications of the product.

The amount of alloy to be added to a given heat is usually expressed in terms of the silicon analysis of the steel. For example, it has been customary to add 0.06 to 0.10 percent silicon as the silicospiegel, etc., as determined by the weight of the charge and the analysis of the alloy. In general, this automatically determines the manganese content, inasmuch

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as the ratio of manganese to silicon in the alloy is 4:1 or 5:1; hence the manganese content would range from 0.24 to about 0.50 percent.

Most of the data which have been obtained concerning the benefits resulting from the use of silicospiegels, silicomanganese, etc., have resulted from the application of these alloys to axle-grade steels (155) ranging from 0.40 to 0.50 percent carbon, 0.50 to 0.30 percent of manganese, and 0.10 to 0.20 percent silicon. Two standard practices were in use in the plant in which these heats were made. In one process large additions of ore were made to the furnace to reduce the metalloid contents to low figures as rapidly as possible, followed by the addition of pig iron, ferromanganese, and ferrosilicon in the ladle to deoxidize the steel and obtain the desired specifications. In the other process, the steel was made under less-oxidizing conditions and deoxidized with Alsifer (an alloy of aluminum, silicon, iron, and titanium) in the ladle. Seams and ghost lines were present in steels produced in these processes, and it was the hope of the investigators to remove these undesirable factors.

The seams present in the steels produced by the old process were determined to be caused by the presence of silica, alumina, and aluminum silicate inclusions, whereas the ghost lines were nearly always associated with the presence of sulphides. It was hoped that the use of silicospiegel would eliminate the silicate stringers and the necessity for using aluminum as a deoxidizer and therefore eliminating the alumina particles. The procedure used in making these heats in which the alloy was added was as follows:

The charge usually was 60 percent pig iron and 40 percent scrap, with just enough ore to give a suitable flush slag. The iron oxide content of the slag in virtually all the heats was approximately 20 percent FeO + Fe_2O_3. The furnaces were fired with natural gas and coke-oven gas and the slags in nearly every instance were quite fluid. No ore was added to the heats after the carbon content had been reduced to 30 or 40 percent above the specifications of the finished steel, thus preventing the presence of an excess amount of iron oxide at the time of the alloy addition.

The alloy was added in virtually every instance 20 minutes before tapping. The heats averaged 150,000 pounds in weight, and two series of heats were made, in one of which 2,500 to 3,000 pounds of high-silicon spiegel were added, corresponding to a silicon addition of 0.08 to 0.09 percent, and in the second series 3,500 to 3,900 pounds of the alloy was added, corresponding to a silicon addition of 0.10 to 0.11 percent.

In every heat it was necessary to add a small amount of ferromanganese to bring the manganese content within the specifications of the steel. The ferromanganese was added in the furnace, and the time schedule on the deoxidation with high-silicon spiegel and this secondary manganese addition was held as close as possible to 10 minutes between the high-silicon spiegel addition and the ferromanganese addition and 10 minutes between the ferromanganese addition and tapping. The best results were obtained with the higher addition and for this grade of steel has resulted in the recommended

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practice. The chief advantage in using the larger addition is that there is less FeO in the metal at the time of tapping than in the other case.

In most of the heats it was essential to add some ferrosilicon in the ladle to meet the desired specification, and because of the lower FeO content much less SiO_2 formed in the heats having the larger addition of alloy.

It was also recommended that fairly high temperatures be maintained toward the end of the heat, and if possible the heat should be held in the ladle to allow for elimination of manganous silicates.

Thickening up the slag immediately after the spiegel addition by means of burnt-lime additions is also an advantage as it prevents diffusion of iron oxide from the slag back into the metal. This can be done by shutting off the furnace gases for a short time, cooling the slag and causing it to become more viscous.

In every heat in which large additions of silicospiegel were made, very few if any seams were found in the finished steel. Inasmuch as it had been previously determined that seams in this particular type of steel were caused by the presence of silicate inclusions, it is obvious that the use of manganese-silicon alloys as a deoxidizer causes elimination of most of the deoxidation products and therefore produces steel which has but few silicate particles present likely to give seams.

Electrolytic analyses were made on all samples and it was found in nearly every instance that the SiO_2 present in the steel was at least 25 percent lower than in the steels prepared by recarburization or Alsifer deoxidation. Other types of steel which have been studied with regard to manganese-silicon alloy deoxidation are low-carbon killed steel, low-carbon rimming steel, and high-carbon seamless tubing steel. The first two grades of material were deoxidized with low-carbon silicomanganese alloys, whereas the latter was deoxidized with a commercial grade of silicospiegel. In every instance decided improvement was obtained when the steel prepared by deoxidation with these alloys was compared to those prepared by standard practices in the various plants.

Probably one of the biggest difficulties encountered in the application of these alloys was concerned with the steel specification itself. Most killed steels being made at present are required to contain a considerable portion of the deoxidizer silicon. In most open-hearth steels the percentage required ranges from 0.1 to 0.2 percent. Electric furnace steels sometimes have a silicon specification as high as 0.3 to 0.35 percent. It is apparent that one of the chief requisites for the successful application of manganese-silicon alloys is that the mechanism of deoxidation as described in these pages should not be disturbed during the deoxidation process.

At the time of tapping a heat which has been deoxidized with the above alloys the steel contains considerable portions of manganese silicates which have not yet been eliminated. If the tapping temperature is high enough the

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metal could be held in the ladle so as to allow these particles to rise to the ladle slag and thereby become eliminated. However, many steel companies will not agree to hold a heat in this manner long enough to obtain these desirable results. Instead, it is necessary to add the silicon to meet the above-mentioned specification and to pour the heat as soon as possible. The action of the silicon addition upon the rising manganese silicate particles can be readily imagined. The MnO present is deoxidized with the added silicon, and the finished steel contains considerable portions of SiO_2 particles, not only from the deoxidation reaction but also the original silica present in the manganous silicate.

Steel specification committees should therefore be shown that the two specifications, "clean steel, containing as much as 0.15 percent silicon", are contradictory. This is true if the "clean steel" is being prepared by the use of manganese-silicon alloys. The purpose of the silicon specification is obviously to obtain complete deoxidation. Deoxidation with silicon alone merely involves the removal of FeO and the formation of the inclusion SiO_2, whereas deoxidation with manganese-silicon alloys involves deoxidation by the reaction of silicon to form SiO_2 and a secondary reaction of manganese to form MnO and subsequent fluxing of these two oxides and their elimination from the steel bath. A "killed" steel may be obtained by either process, but a clean steel can only be obtained by the latter.

Saving of Ferromanganese by Means of Fluorspar in Open Hearth

An interesting suggestion was made by Goldmann (116) which involved the use of fluorspar to save manganese in the open-hearth furnace. This investigator stated that in various heats it was found that manganese was consistently reduced from the slag into the metal by means of additions of this material. The actual mechanism of the saving described by this author is somewhat open to question, but there is a possibility that in the heats studied by Goldmann lumps of lime were floating in the slag at the time of the fluorspar addition. The thinning action of fluorspar on the slag is well known, and the effect of hastening the solution of large lumps of lime in the slag has also been noted. If more lime is taken into solution by this procedure the basicity of the slag is of course increased, and the reduction of manganese from the slag into the metal by this process is more understandable. The basicity of the slag may also be increased by the reaction of fluorspar on the SiO_2 of the slag to form volatile silicon tetrafluoride. This results in an increase in basicity.

Recovery of Manganese from Steel-Making Slags

In 1918 the amount of manganese lost in steel-making slags was estimated to be approximately 114,000 tons (259). Some 10 years later this amount had increased to approximately 279,000 tons, and the increase was attributed not only to the increase in production but also to the practice involving the use of higher-manganese pig iron (151). It was shown that the average MnO content of basic open-hearth slags had increased during this period from 5.5 to approximately 8.5 percent. Many pleas for conservation of manganese to be

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found in the literature have pointed out as one of the possibilities the recovery of manganese from basic open-hearth slags.

It is known that during the late war Swedish manufacturers were confronted with similar scarcity of high-grade ores, as in the United States. Also, it has been pointed out that the situation was partly met through their utilization of blast-furnace and electric-furnace slags. At that time the high-manganese pig irons, which were being made in Sweden, were prepared under a blast-furnace slag containing as much as 20 percent manganese. These slags were placed in electric furnaces and reduced by means of coke and ferrosilicon in such a manner that a fair grade of silicomanganese was obtained which could be used for final deoxidation purposes.

Some Swedish bessemer slags were said to contain as much as 50 percent manganese through oxidation of high-manganese low-silicon pig iron in this process. Sixty percent of this manganese was recovered in electric-furnace processes similar to those described above.

In the United States some manufacturers attempted to recover the manganese from the flush slags in the basic open hearth. As is stated on page 265 these slags contain more manganese than the finishing slags from this process because they are run out of the furnace soon after pig iron is added to the open-hearth furnace. During this same process limestone starts to rise from the bottom of the furnace and tends to dilute the slag and thereby decrease the manganese content. The amount of manganese oxide in slags of this type ranges from 10 to 25 percent. One manufacturer who charged slags of this type into the blast furnace recovered as much as 18 percent of the iron and 10 percent of the manganese from the slag. The manganese recovery is not the only advantage which was recognized through this practice. Inasmuch as the basic open-hearth slag contains considerable portions of lime (30 to 50 percent CaO), 50 pounds of lime were taken from the blast-furnace burden for every 100 pounds of open-hearth slag charged. The silica present in this slag was also found to be advantageous, and in general smoother operation of the blast furnace was obtained.

MANGANESE STEELS

The remainder of this paper will be concerned with the influence of manganese upon the properties of solid iron.

In 1882 the researches of Hadfield (136) resulted in the discovery of the peculiar and remarkable properties exhibited by steel when it contained large percentages of manganese. The ordinary properties and nature of the iron were completely changed by such additions of manganese (10 to 15 percent).

Before Hadfield's development of manganese steel there had been just 1 or 2 special manganese products, including the Mushet self-hardening steel, which was rather brittle and useful only for tools.

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In 1906 the eminent French metallurgist Leon Guillet (128) proposed the well-known diagram of the constitution of iron-manganese alloys in which all steels above a line connecting 14 percent iron and 1.65 percent carbon consist of austenite. Later research by Howe, Campbell, and Hall (144) showed that Guillet did not take into account the presence of cementite in the austenitic steels when the carbon content was above 1 percent. These investigators added the modifying lines XY and WZ of figure 51. Steels whose composition lies between these lines consist of pure austenite when quenched from temperatures slightly above 1,000° C. If carbon is above the line WZ, the equation of which is $C = 1.075 + \frac{0.1\ Mn}{3}$, free cementite will be found in the steels even after quenching. When carbon falls below the XY line, whose equation is $C = 1.075 - 0.04\ Mn$, the steels will contain both martensite and austenite after quenching, therefore the range of useful austenitic manganese steels is considerably narrower than the original Guillet diagram suggests.

As the diagram indicates, there are three principal groups of manganese steels: (1) Pearlitic; (2) martensitic; and (3) austenitic. The various lines converge on 1.65 percent carbon from 5 percent manganese in the pearlitic field and 12 percent manganese in the martensitic field. There is a slight area between each field where there is gradual transition from one form to the other, and both constituents will be found in steels whose compositions fall within such transition ranges.

Neville and Cain (273) have shown that addition of manganese to carbon-free iron affects the properties of iron very slightly. However, as soon as carbon is introduced in conjunction with manganese the influence on the mechanical properties is quite evident, according to the amount of each element present. Each element augments the effect of the other up to certain limits of composition.

Pearlitic Manganese Steels

These steels have been steadily gaining favor in recent years because of certain metallurgical, mechanical, and economical advantages, even though formerly a manganese content greater than was absolutely necessary for the maintenance of sound metal was generally discouraged by users of special steels. The former ill repute of this class of manganese steel may be traced to lack of knowledge concerning the importance of controlling composition, manufacture, pouring, and rolling (171,371).

A manganese content of 1 percent is equivalent to 2 percent nickel in its effect on the physical properties of iron (101). Manganese, acting similarly to nickel, raises the tensile strength and elastic limit of steel considerably without decreasing the toughness. Consequently, by maintaining a comparatively low carbon content and increasing the manganese to the vicinity of 2 percent, the strength will be equivalent to that of a high-carbon steel without the sacrifice of ductility.

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The carbon content of the steel should be selected in accordance with the manganese content and the future use of the steel. The steels most commonly found may be divided into several types (102):

Steel type	Percent			
	C	Mn	P	S
1	0.10-0.20	1.20-1.50	0.04 max.	0.075-0.15
2	.15- .25	1.00-1.20	.045 max.	.045 max.
3	.25- .35	1.35-1.75	.05 max.	.075-0.15
4	.30- .40	1.35-1.75	.05 max.	.075-0.15
5	.45- .55	1.10-1.30	.045 max.	.045 max.
S.A.E. 1350	.45- .55	.90-1.20	.04 max.	.055 max.
S.A.E. 1360	.55- .70	.90-1.20	.04 max.	.055 max.

The manganese specifications for the various types depend primarily upon the thermal treatment the steel is to undergo and the mass of material entering into such treatment.

Heat Treatment

Low-manganese steel heat treatment is similar to that of other pearlitic types. Even though manganese does lower the critical temperature somewhat over a straight carbon steel the manganese absorption above the critical is slow, and the heat-treating temperature should not be lowered because of the high manganese content. If the section or casting is heavy and is to be given two heat treatments the first should be somewhat above 900° C. to break up the as-cast structure and completely homogenize the material. The second treatment may be around 850° C. to refine the grain structure.

Uses

Types 1 and 2 (102) may be hardened with a very hard surface at low temperatures and at the same time have a very strong core so that these steels are commonly used in case-hardened parts like cam shafts, roller bearings, gears, etc. Careful heat treatment of these parts after carburization is quite essential to obtain the highest quality product. A double heat treatment after carburizing is recommended; this consists of: (1) Refining and toughening the core by reheating and cooling in carburizing boxes to 840° to 870° C., then quenching in oil; and (2) refining the case by again reheating to 755° to 775° C., then quenching in oil. A final tempering at 150° to 260° C. is desirable when the case is ground, as this prevents grinding checks.

Type 3 and 4 (102) pearlitic steels are used for parts such as heat-treated shafts, spindles, and gears where high strength and toughness are required in conjunction with good machining qualities. Heat treatment for these classes consists of quenching in oil from 830° C. and tempering between 750° and 1,050° C., depending on the combination of hardness, strength, and

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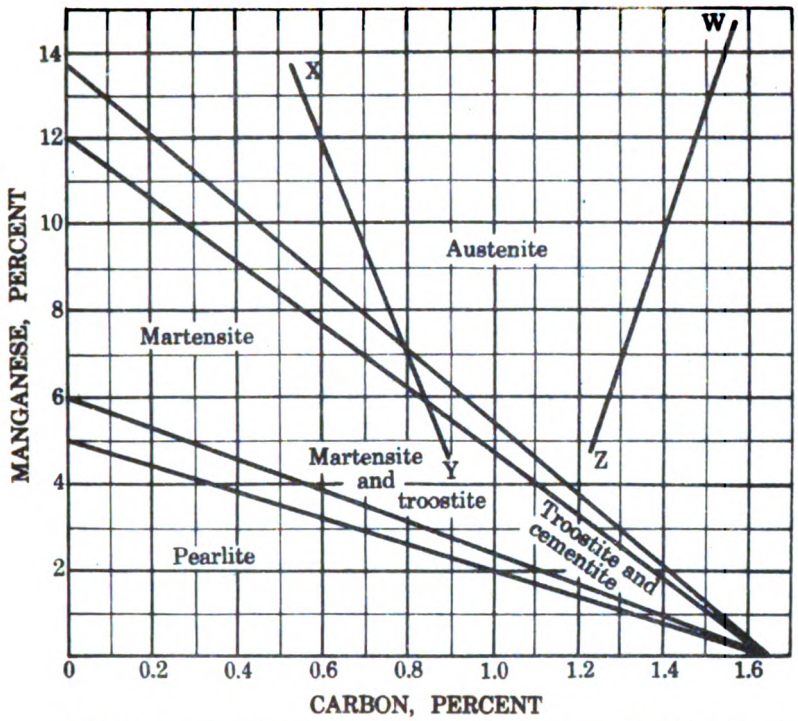

Figure 51.- Modified Guillet diagram summarizing constitution of iron-manganese alloys.

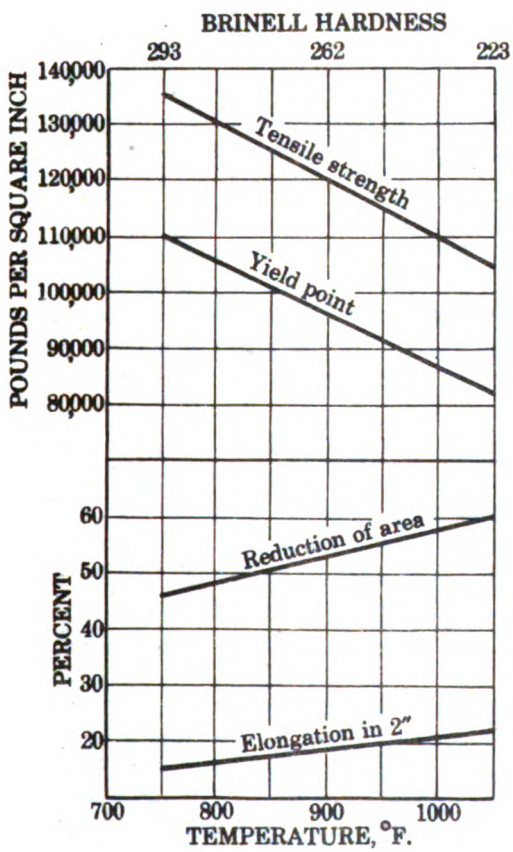

Figure 52.- Physical properties of manganese steel, type 3.

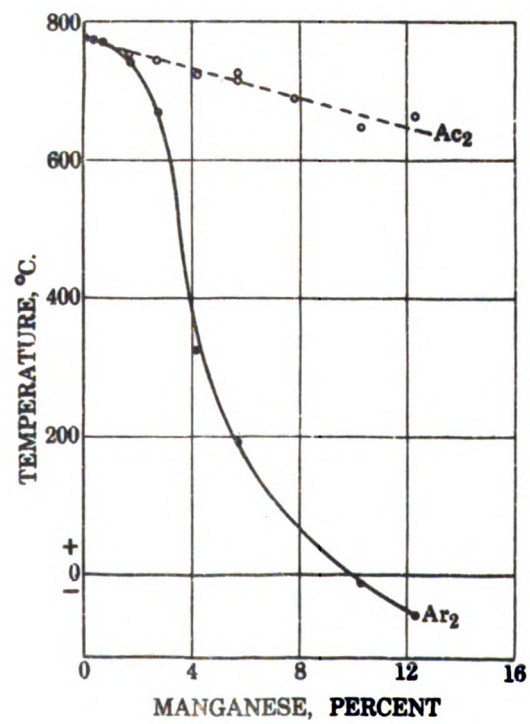

Figure 53.- Magnetic charge in manganese steels (Gumlich).

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toughness desired in the finished part. Low tempering temperature results in high tensile strength, yield point, and hardness, with low elongation and reduction of area, high tempering temperature resulting in contrary results. Figure 52 shows this influence of tempering temperature on properties.

Type 5 (102) manganese steel is used where physical properties must be of quite a high order, such as clutches, bolts, gears, and shafts. The steels are quenched from 800° to 815° C. and tempered to the desired hardness.

Steels 1350 and 1360 (102) of S.A.E. specification are used for helical springs made from round cold-drawn wire up to three-sixteenths inch in diameter.

In general, pearlitic manganese steels offer no particular difficulty in the manufacture of parts which need to be welded during fabrication. Also, they may be forged in any regular forging operations. These steels may be cold-drawn into wire if properly annealed before drawing.

A steel containing 0.80 percent carbon and 2.00 percent manganese is quite suitable for use as a shear blade in cold-cutting steel bars. It is claimed that this steel gives longer service under similar conditions than any plain-carbon or chromium-vanadium steel of equal carbon content. Masses weighing 500 pounds may be hardened without any difficulty.

The lower-manganese type of pearlitic steels is virtually equivalent to bessemer screw stock in machining qualities, but, as may be expected, machining difficulties increase as carbon and manganese are raised.

Pearlitic manganese steels are appreciably more resistant to sea water and most natural water corrosion than are the ordinary carbon steels. This has resulted in widespread application of a 0.35 percent carbon and 1.35 percent manganese steel in the manufacture of cast-steel anchor chain. It renders good service because of its combinations of corrosion resistance and high strength and ability to withstand suddenly applied stresses.

In the as-rolled and normalized condition these steels are used for steel rails. Standard open-hearth steel rail is measurably improved by lowering the carbon to 0.55 to 0.70 and increasing the manganese to 1.25 to 1.50. If carbon and manganese are both on the high side the rail will be too brittle, while both elements on the low side would give a rail which probably would flow under traffic. By properly balancing the two elements, a long-wearing, tough, generally satisfactory rail is obtained.

Ship and boiler plate, high-strength structural steel, compressed-gas cylinders, and seamless steel tubing, in some of which the manganese approaches 3 percent with correspondingly lower carbon percentages, are further applications. Also, for specialized applications varying percentages of other alloying elements such as nickel, chromium, molybdenum, and silicon often are added to these pearlitic manganese steels. They have not received general application, even in view of their excellent physical properties,

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because the manufacturing difficulties encountered in forging and machining operations increase the fabrication cost considerably.

Advantages

These steels are quite applicable in many instances where a superior quality of material is desired and still the expense of a high-priced alloy steel would be prohibitive for the particular use for which the steel is required. The advantages of using pearlitic manganese steels are threefold: (1) Metallurgical; (2) mechanical; and (3) economical.

The metallurgical advantage lies in the lower carburizing temperatures and carburizing time and the uniformity of properties after thermal treatment. and decreased danger of deformation on such treatment.

Mechanically these steels show good physical properties and better resistance to abrasion because of their high hardness and toughness.

Economical advantages include 20 to 90 percent speed increase in mechanical operations, less straightening work because of less distortion in heat treatment and 35 to 40 percent longer life of tools.

Martensitic Manganese Steels

As shown on the diagram of figure 51 there is a triangular area covering a considerable range of manganese and carbon contents which is designated martensitic. This region extends from about 5 to 12 percent manganese with low carbon. With increasing carbon content smaller amounts of manganese will produce the same structure. Thus with 0.8 percent carbon, about 3 percent manganese will produce martensite and troostite.

Steels of this class have received no industrial application due to their extreme brittleness, some of them disintegrating to powder under the shock of a hammer. In the cast condition these steels are especially brittle -- in fact, their brittleness is virtually equivalent to that of glass. It is possible to increase the strength somewhat of some martensitic compositions by light hammering or forging, but even after such treatment the product is so brittle that it is commercially useless.

Austenitic Manganese Steels

This important and useful class of steels containing manganese is the result of the classic researches of Hadfield (136) in the early eighties on the influence on the ordinary carbon steels of his day of increasing the manganese content. Previous researches on the effects of manganese additions showed that manganese over 2.5 or 3.0 percent in steel resulted in a metal that was brittle and practically useless. The obvious conclusion followed that there was no sound reason to suppose higher percentages of the same embrittling element would cause any change in this condition. However, Hadfield was unwilling to take the apparently obvious for granted and continued experimenting with increasing additions of manganese.

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Hadfield found the same condition of hardness and brittleness in the range of manganese between 2.5 and 7.0 percent at the carbon contents with which he was working. However, above 7.0 percent manganese the steels started to undergo remarkable changes depending on casting temperature and other considerations in physical properties; brittleness and extreme hardness disappeared, strength and ductility increased, and the metal became nonmagnetic. Such remarkable properties, which were diametrically opposed to those of ordinary steel, heralded the appearance of a remarkable discovery and served as the impetus for development of alloys of other elements with carbon as well as the ternary manganese alloy.

The Guillet diagram for alloys of iron, manganese, and carbon, as modified by Hall (144), shows that true austenitic steels will not be obtained by merely having 12 to 14 percent manganese, a corresponding carbon content of 0.6 to 1.2 or 1.3 percent being necessary also. (See p. 293 of this paper.) In fact, the standard austenitic or Hadfield manganese steels contain 11 to 14 percent manganese and 1.0 to 1.3 percent carbon, which falls well within the austenitic range specified by Hall. These steels also contain 0.3 to 0.8 percent silicon and 0.05 to 0.08 percent phosphorus.

Manufacture

Austenitic manganese steel until recently was made in the bessemer converter using a low phosphorus and sulphur cupola metal which was blown soft to between 0.10 and 0.25 percent carbon. To this low-carbon metal molten ferromanganese was added in sufficient amounts to produce a manganese steel containing 11 to 13 percent manganese. The steel was blown quite hot and held just a few minutes for mixing in the ladle before pouring. Such metal was similar in quality to ordinary converter steel in carbide conditions and oxide content.

The disposal of manganese steel scrap presented quite a problem in this process because a metal made from old scrap was rather irregular in composition, and purchasers refused to buy it.

The basic electric furnace (170) offered a solution to the problems of converter practice. First is its absolute power of deoxidation, which is effected under heavy lime slag with a minimum loss of manganese. Also, the metal may be held any length of time without excessive changes in composition, awaiting the results of chemical analysis and thus making regular analyses possible. In addition, the temperature may be controlled closely without resorting to holding the ladle, a practice that might contaminate the metal with slag resulting from corrosive action of the metal on the ladle refractories. Finally, the electric furnace can make satisfactory metal by remelting manganese-steel scrap without any appreciable loss of manganese.

Because of its high manganese content manganese steel attacks the ladle lining, causing considerable slag to form during pouring of the heat. This slag will cause defects in the steel if not carefully held back during

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casting. Special tea-spout ladles have been devised for this purpose.

Properties

These steels have the following peculiar characteristics:

1. The alloy may be water-toughened by drastic quenching from red heat. This property, which combines a ductility resembling that of mild steel with a high degree of elasticity, enabling it to withstand shocks that would cause complete failure in ordinary steel, is in exact contrast to carbon steels, which are made comparatively brittle by the same procedure.

2. Even though the steel contains about 86 percent iron, it is non-magnetic.

3. The tensile strength, combined with extraordinary elongation (50 to 70 percent), exceeds that obtainable with the purest iron.

4. The resistance of the steel to abrasion is greater the more severe the service to which it is applied.

The particular properties of these austenitic steels depend upon the treatment given them, this treatment in turn being determined mainly by the use for which the steel is intended. They may be used in the condition as (1) cast, (2) forged, and (3) rolled, the water-toughening treatment being applied in each instance. Austenitic manganese steel greatly resembles cast iron in regard to its fluidity and ability to fill molds of intricate shape, provided full allowance is made for its rather great shrinkage.

Cast-manganese steels, after suitable treatment, possess an extraordinary combination of hardness and toughness which enables them to withstand abrasion quite satisfactorily. This hardness of toughened manganese steel is rather unique and has been termed a tough hardness rather than a flinty hardness. It is a hardness that is peculiar in that it is not practical to attempt to machine or drill it, and yet it may be easily dented by a hammer or marked with a chisel or file. It also has a peculiar flowage when used in crushing machinery, during which the abraded area becomes hardened and still retains the tough austenitic backing under the hardened surface. As this surface gradually wears away subsequent impacts harden another layer of material, and the process continues throughout the life of the casting.

Austenitic manganese steels, like plain steels, are improved in physical properties by hot-working, such as forging or rolling (88,240), even though it is difficult to roll them into anything but simple, plain forms. However, by careful manipulation and control of the steel and proper heat treatment rails, sheets, plates, and even complicated assemblies such as rail crossings may be produced successfully. Usually it is essential for the ingot to be rolled or hammered all over very lightly at first and returned to the heating furnace again before much reduction of size is attempted. The range of temperature within which the steel may be rolled is rather

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narrow, because if it is heated too hot it will crumble and if it is too cold it will burst the housings of the rolling mill.

The forging operation must be controlled carefully. A steel which has been well worked or rolled, with proper subsequent heat treatment, will have a tensile strength of 140,000 pounds per square inch and 50 percent elongation in 8 inches compared to the same steel cast and toughened with a strength of 80,000 pounds per square inch and 20 percent elongation. A cold-rolled manganese steel has shown strengths of 250,000 pounds per square inch, but the ductility in this condition is very low.

Manganese steels have a high coefficient of expansion which must be fully considered in designs for castings and in heating steel for the toughening treatment. The castings, which are freer of blowholes than ordinary steel castings, should be so designed that the mass is fairly uniform throughout or that no part is much thicker than any other section because of the liability of the casting being cracked or pulled apart on cooling due to considerable contraction. The poor heat conductivity tends to limit the thickness of sections that may be profitably heat-treated. This limit is usually placed at 4 inches, although slightly thicker sections, in which the presence of internal cracks in the central portion are not ruinous are sometimes heat-treated. If the furnace is much hotter than the piece placed in it for heating the low heat conductivity of the metal retards the passage of the heat to the interior, and the temperature of the skin rises rapidly, and due to the high expansion coefficient the exterior of the piece is expanded so quickly that the interior is likely to become cracked.

A most remarkable property of manganese steel is its lack of magnetic permeability and susceptibility, in spite of the fact that it contains about 85 percent of metallic iron. Moreover, the electrical resistance is about 30 times that of copper and 5 times that of wrought iron. The explanation for this nonmagnetic condition is that the high percentage of manganese contained in the metal prevents the molecular structure from aligning itself into paths of flow for magnetic lines of force.

Influence of Manganese on Magnetic Properties of Steel

The magnetic susceptibility (347) of manganese at room temperature for 99.9 percent manganese is 7.55×10^{-6}. This susceptibility increases abruptly at 810°, the $\alpha - \beta$ transformation, and undergoes another magnetic susceptibility increase at the $\beta - \gamma$ change.

The addition of nonmagnetic manganese to an iron-carbon alloy or steel causes gradual decrease in magnetic properties, until at a manganese content of 13 percent ordinary water-toughened austenitic steel is practically nonmagnetic. Steels with manganese contents between 2 and 13 percent show a decided hysteresis effect in the magnetic transformation on heating and cooling. This hysteresis is rather pronounced between the Ac_2 and Ar_2 transformation points. The magnetic properties of manganese steels as incidated

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by figure 53 show that a 10 percent manganese content (carbon, 0.1 to 0.2 percent) requires cooling below 0° C. before magnetism is recovered if the alloy has previously been heated above the Ac_2 point.

Hadfield and Hopkinson (141) could find no simple relation between the proportion of manganese and the reduction in magnetism in iron-manganese alloys. They did find that the lowering of magnetism by manganese is affected by small amounts of carbon, but they also noticed other anomalies attributed to the temperature to which the samples were subjected during forging and rolling.

Table 87 illustrates the effect of carbon and manganese on magnetic saturation.

TABLE 87. - Effect of Carbon and Manganese on Magnetic Saturation

Sample no.	Analysis, percent			Relative magnetic saturation, percent (pure Fe = 100)
	C.	Si.	Mn	
37	0.08	0.130	3.50	90.9
38	.15	.370	5.40	93.6
39	.16	.630	10.08	44.5
40	.15	-	15.27	4.5
41	.41	.070	2.23	95.0
42	.78	-	3.81	54.3
43	.36	.100	4.68	91.6
44	1.00	-	7.00	74.0
45	1.66	-	11.53	42.0
45	1.66	-	11.53	41.5
46	1.66	-	11.53	2.0
47	1.23	-	12.64	-
48	.26	-	13.00	15.0
49	1.50	.14	15.22	8.5
50	1.54	-	18.50	0.0

In No. 38, 5.40 percent manganese acts like an inactive diluent, while in No. 37, with low carbon, the percentage reduction is three times the percent manganese. An additional 5 percent manganese caused a 50 percent reduction in magnetism.

Hadfield and Hopkinson found that by heating the nonmagnetic austenitic alloy to 520° C. for a long period the steel has an amount of magnetism corresponding to about two thirds that of pure iron. The material could be rendered magnetic by heating below 520° C., but the change was much slower. Heating above 700° C. rendered the material only slightly magnetic.

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On the destruction of this magnetic quality by heat treatment, any temperature of heating below 550° caused no diminution of the magnetism, but it is diminished by heating at 640° C. or above. A few minutes heating at 750° C. virtually destroys the magnetism, if the steel is cooled either by quenching or by air.

Hardness

Manganese steels owe their great wear-resisting qualities to the conditions which Hadfield (138) expressed as a "peculiar hardness combined with a special kind of softness", which in reality is a combination of hardness and toughness or ductility, producing certain results under definite conditions of deformation or abrasion. Castings or forgings (284) of these steels are too hard and brittle for practical use, due to deposition of a double carbide of manganese and iron in an acicular form. Reheating to bright-red heat and quenching in water reconverts this precipitated carbide into the crystalline or so-called gamma solid-solution state, with a hardness of slightly over 200 Brinell and the ductility which renders it so valuable. The toughness it possesses in greater measure than any other metal is due to its very closely knit, cohesive grain structure, the result of proper water toughening. When this steel is subjected to wear either abrasive or incisive the structure knits together even more firmly than in its unworn state, enabling it to resist abrasion or cutting.

This remarkable abrasion resistance is explained by the somewhat unstable crystalline condition of the metal. Any steel, when heated above its critical temperature, passes into a nonmagnetic, gamma iron, austenitic state. Most alloying elements, including carbon up to 1.7 percent, are soluble in gamma iron. Even severely quenched steel cannot be retained in the gamma condition unless some obstructive element is present. Manganese content of 10 to 14 percent with 1.0 to 1.5 percent carbon acts as such an obstructive element. When the steel is heated to about 1,040° C. the same nonmagnetic austenitic structure is obtained. The high manganese content obstructs the gamma to alpha change and the precipitation of iron carbide, and by rapid quenching the mass is maintained in an austenitic condition but in a somewhat metastable state.

This quenched, strong, tough, austenitic steel is so unstable that cold work or even impact will cause some gamma to alpha transformation with precipitation of carbon. This unique property of surface hardening under mechanical deformation makes the steel valuable to industry. The hardening from about 200 Brinell to as high as 550 at point of abrasion or impact is the secret of the durability of the austenitic manganese steels.

The best wear-resisting qualities are obtained under the hardest working conditions. Its hardness during machining is due to the deformation produced during the cutting action and pressure of the tool, which in its turn causes increase of hardness and causes the machining process to be impractical.

The same conditions explain the difficulty encountered in drawing manganese steel into wire, the passage through the dies causing the hardness following mechanical deformation.

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Heat Treatment

The unique and useful properties of austenitic manganese steels depend even more on the heat treatment and cooling to which they are subjected to develop the great toughness and ductility than the highly important consideration of composition of the steel. These steels show the distinct characteristic that quenching and annealing produce effects opposite to those obtained in most other steels, quenching making the alloy tough, ductile, and non-magnetic, while annealing makes it hard, brittle, and partly magnetic.

To obtain maximum toughness and ductility, manganese steels are quenched in water from a high temperature, but the rate of heating, maximum temperature, and rate of cooling may be varied considerably without changing the results materially. Thus while in ordinary steels the heat treatment is guided more or less by transformation temperatures, high-manganese steels have no critical points, so that the only criterion of the proper temperature is the relation of the carbide to the physical properties. The absorption, with or without the precipitation of such carbides, is the underlying basis for heat treatment adjustment.

The thermal treatment for these steels involves two distinct factors: (1) The change of grain size; and (2) the relationship of austenite and carbide, with or without the presence of martensite. Martensite may be omitted, since commercial manganese steels do not naturally contain it.

The necessity for the first consideration is obvious. Manganese steel as cast is fundamentally austenitic, the crystals often being excessively large and in many instances forming a weak, columnar structure. Forged manganese steels may have fine grain structure and still be weak and brittle. Annealing would cause grain refinement but is illogical, because it has an injurious result on the steel — the formation of the maximum amount of carbide, an extremely hard, brittle manganitic cementite rejected by the austenite, which forms a weak membrane around the austenite grains as spines and needles.

Heating to high temperature causes the membrane of double carbide of manganese and iron, or carbide segregation, produced by cooling after casting to be taken into solution gradually by the austenite, and by rapid cooling this carbide is more or less prevented from reprecipitation. The temperature of heating must be high (about 1,050° C.) and the cooling drastic, such as water quench, to give the most ductile steel.

When castings undergo some heating after having received the water-toughening treatment carbide precipitation occurs if the temperature goes over 390° C. impairing its ductility and wear-resistance properties. Temperatures below 390° C. may be accommodated without losing any of the remarkable ductile properties. If heating has been carried near the danger point it is advisable to take it to 1,050° C. and requench.

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This embrittling effect due to destruction of austenite by precipitation of carbides when the steel is heated above 390° C. proves valuable in the recovery of large pieces of manganese-steel scrap. It is merely necessary to heat to a slight red and cool slowly in the furnace; then the section can be broken as easily as cast iron by means of a drop ball.

Uses

The extreme difficulty encountered in machining the austenitic manganese steels has limited their use considerably. The steel is usually applied in such conditions where the castings or forgings can be used without further machining. Sometimes a final finish is given by grinding.

Manganese steel receives wide application in uses requiring resistance to abrasion under slow speeds of impact, such as in rolls, crushers, and car wheels running at slow speeds (on mine cars, for example). Moreover, for railway-track frogs, switches, and curved rails the steel is used extensively. Manganese-steel rails abrade more slowly on sharp curves than bessemer or open-hearth steel rails.

The steel is an ideal material for burglar-proof vaults and safes. In carbon or chromium steels the burglar's blow pipe will draw the temper locally by simple heating so that as soon as it is cooled the metal can be drilled and the dynamite charge introduced. Such treatment does not soften manganese steel but makes it harder. Also, the steel is too strong to be broken by dynamite and nitroglycerin.

Because of its nonmagnetic property the steel is employed for cover plates of lifting magnets handling heavy iron and steel articles where it is subjected to hard blows of the pieces attracted to the magnet. It offers virtually no obstruction to the passage of the magnetic attraction. The steel is also used around the structure of the compasses on ships because it does not affect the compass needle. Railway switches and diamonds are covered with a layer of manganese steel by arc-welding a 13.8 percent manganese and 1.23 percent carbon steel on the rail. After being worn down it can be refilled. Adherence is improved by drilling holes at an angle into the rail.

This steel is most applicable for use in equipment employed in the mining, milling, and treatment of ores and other mineral products, quarrying and rock dressing, digging and dredging, or parts of machines exposed to gritty wear. Mere hardness is not the only quality desired for these purposes, for in that instance chilled iron would be the logical material, whereas manganese steel, which is not as hard as chilled iron but has the added property of being as tough as mild steel, will wear as much as 4 to 7 times as long in this type of service.

It is common belief that austenitic manganese steel must be as low as possible in carbon to attain maximum ductility, the manganese : carbon ratio being as high above 10.00 as can be obtained. However, a comparison by Barton (15) of three series of compositions which were above the minimum ratio number had quite different ductilities.

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	Average content, percent C	Mn	Ratio, Mn : C
Series I	0.96	10.94	11.40
Series II	1.05	11.61	11.00
Series III	1.22	12.74	10.40

Series III bent cold on the standard bar test 180° without cracking. Series II bent only about 120° before incipient cracking. Series I began cracking at 90°. Therefore, although the steels all fall within the chemical specifications, a steel of lower quality than might be desired for some purposes sometimes results. Therefore, for parts where extreme ductility and resistance to shock are desired, a manganese content between 12.50 and 14.00 percent should be specified.

A special application (137) which resulted in the saving of many lives was found during the World War in which, due to its high tenacity and ductility, it was used in body shields and helmets. This high tenacity, combined with extraordinary elongation, enabled shields of manganese steel to resist penetration of bullets by bulging rather than penetration, the material taking up the impact by indenting gradually and thus offering a larger surface of resistance.

Due to its great toughness and tensile strength, which practically eliminate breakage, rolled manganese-steel plate is used for dipper doors on shovels for crushed stone-quarries. The pieces handled are large and heavy, causing considerable wear and breakage when any other steel is used on the dipper doors. Woven screens of manganese-steel bars give a life many times that of screens made of soft ordinary steel. Coke acts as though it contained many minute diamonds, which rapidly wear away the metal on which it impinges.

If the cost, due to the hardness developed during the process of drawing into wire, were not so great, manganese steel would be an excellent resistance material in the form of wire because of its high electrical resistance, its specific resistance ranging from 65 to 75 microhms per cubic centimeter. It does not wear so well when used with sharp easily friable materials, because such use does not harden the surface enough.

Because of its low yield point, manganese steel does not give satisfaction in many lines for which it would otherwise be fitted. If the pressure at the point of wear passes the flowing point the results are unsatisfactory, though even then they may be better than those from the use of other material.

MANGANESE IN CAST IRON

Cast iron is an alloy of iron, carbon, and silicon, in which the carbon is so high — over 2.2 percent — that the alloy is not malleable as cast at any temperature. Bolton (29) has classified cast iron as follows:

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1. Pig iron.
2. White cast iron:
   (a) Chilled iron.
   (b) Malleable iron.
      (1) American or black heart.
      (2) European or white heart.
3. Gray cast iron.
   (a) Ordinary gray iron.
   (b) Semisteel.
4. Special irons.
   (a) Pearlitic iron.
   (b) Mottled iron.
   (c) Alloy iron.

Pig Iron

Manganese tends to increase the total carbon content of pig iron by forming stable carbides, provided the manganese content is higher than that necessary to combine with the sulphur to form MnS. The excess manganese forms a double carbide, $(FeMn)_3C$, and thereby increases the proportion of carbon in the combined form and also results in higher total carbon in the pig iron. Sulphur has an equivalent effect of increasing combined carbon content, but when present with manganese the two elements combine to form MnS and thereby neutralize each other as far as increasing combined carbon is concerned. Consequently, when manganese is high in pig iron an increase in sulphur will decrease the amount of $(FeMn)_3C$ and thereby decrease the tendency of manganese to raise combined carbon as well as total carbon.

With the exception of direct metal used as a hot addition to a steel-making charge, blast-furnace iron is cast into pigs and later either is remelted and cast, producing gray and white cast irons, or is refined in the steel-making process.

White Cast Iron

White cast iron contains almost all of its carbon in the cementitic or combined form. The iron may be obtained in two classes — chilled or malleable — depending on the casting procedure or treatment given after casting. Casting the iron against metal chills produces the chilled variety of cast iron.

Low manganese content will have little appreciable effect, silicon and sulphur having greater influence, on the chill cast iron produced because it merely acts as a deoxidizer and desulphurizer, cleansing the metal from impurities, and greatly increasing the strength and ductility of the casting without injuring the chilled section. When alloyed in higher percentages — 2 percent or more — in the presence of silicon, the manganese exerts a stabilizing effect on the eutectic cementite, producing a hardening and chilling effect of a coarse, crystalline nature.

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Manganese increases the shrinkage of white-iron castings because of the tendency for manganese to retain carbon in the combined form. Additions of enough silicon to cause graphitization of some of the cementite decrease the shrinkage considerably. The hardness of white cast iron is increased by manganese, which hardens both by increasing the combined carbon and also by forming an iron-manganese carbide, $(FeMn)_3C$, which is quite hard.

The malleable variety of white cast iron is further subdivided into two classes, depending on the treatment after casting. The European treatment gives the so-called "white-heart" malleable castings, while the American process is modified to produce the "black-heart" castings. The metal must be of such composition that it is just on the line between the precipitation of graphite and its retention in the form of cementite and dissolved carbon. In all instances the majority of the carbon must be dissolved or combined. The castings are reheated to 625° to 875° C. and maintained at this temperature for 60 hours, which precipitates graphite as temper carbon or temper graphite.

White-heart castings are made by the same method, but the annealing is prolonged until the pieces are practically decarburized to the core as well as on the surface.

The manganese content in malleable cast iron must be confined within certain maximum amounts. Manganese must be twice the sulphur content; even three times is preferable, except when the sulphur content is 0.3 percent or more. Some authorities set the limit for manganese at 0.3 percent. However, 0.5 percent of manganese aids in decreasing checking; also it protects silicon from oxidation both during melting and during annealing, and on this account aids in completing precipitation of the temper carbon in the malleable castings. The manganese should never exceed 0.6 percent in this grade of cast iron, as it makes the casting hard and difficult to machine or anneal.

Gray Cast Iron

Ordinary gray cast iron is so designated because of its characteristic gray fracture. Its composition is such that none of the carbon is retained as free cementite but is present as a constituent of pearlite or as graphitic carbon flakes. Proper decomposition of the combined carbon in massive cementite is accomplished by adjustment of the silicon content. Just enough should be present to accomplish graphitization of free cementite but not affect the pearlite.

As gray iron depends on proper graphitization, manganese should be maintained within certain limits which will not have too great a carbide-stabilizing effect on the graphitization influence of silicon. Manganese has been considered to assume several forms, such as manganese carbide associated with cementite in the pearlite of the cast iron and manganese sulphide which occurs as small rounded particles throughout the metal. Manganese content in ordinary commercial ranges has very little influence on the properties of gray iron.

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The slight influence of manganese on gray cast irons is an increase in tensile and transverse strengths up to about 1 percent manganese, above which the strength again decreases. Hardness also increases with manganese content. However, when the manganese is low the hardness remains virtually the same because of greater graphite separation, as small amounts of manganese up to 0.3 percent increase the graphite separation in gray castings containing about 1.5 percent silicon. Further increase of manganese to 2.5 percent does not affect the separation of graphite.

The effect of increasing manganese content on shrinkage is not so great in the gray iron as in the white cast-iron product because of the formation of some secondary graphite during cooling.

The semisteel variety of gray cast iron is merely a gray iron which has been diluted with some steel scrap, thereby lowering the content of silicon, phosphorus, and total carbon. These lowered compositions result in the graphite being distributed in a fine state of division in the purest possible form of pearlite. Fairly high manganese, combined with low carbon and silicon, is responsible for attainment of the desired fine-grained structure.

Special Cast Irons

The special irons, such as pearlitic irons, high-strength irons, and alloy cast irons, are not greatly influenced by manganese content, their particular properties being obtained by proper casting, adjustment of carbon content, or addition of the alloying elements nickel, chromium, vanadium, and molybdenum. The manganese content of these special irons is merely maintained within the ordinary commercial range of 0.35 to 0.90 percent.

General Effect of Manganese on Cast Iron

Manganese lowers both the temperature of primary solidification and the eutectic temperature of the iron-carbon system. The latter temperature is gradually lowered to 1,120° at about 13 percent of manganese. Above this amount the solid solubility increases and the melting point is gradually raised to 1,260° C. at 80 percent of manganese.

The eutectoid temperature is not changed very much by manganese. However, by increasing the hysteresis the temperature at which inversion occurs is greatly affected. Each percent of manganese lowers the Ar_1 transformation point of iron-carbon by 20° to 25° C. (1). The pearlite becomes finer up to about 5 percent manganese. Above this amount the gamma solid solution remains undecomposed down to room temperature. The effect of manganese on cast iron containing silicon, as it ordinarily does, is somewhat modified by the silicon. It has been shown that 2.50 percent silicon is enough to precipitate graphite in the presence of 16 to 18 percent manganese. Also, manganese does not lower the freezing point of the iron, but the Ar_1 point is lowered even more rapidly than in the low-silicon or white iron series. The pearlite point disappears at about 4 percent manganese and is an explanation as to why high manganese produces hard, white cast iron. Moreover, the gamma solid solution

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appears before graphite disappears, tending to make iron white.

Manganese exerts a detrimental effect on the magnetic properties of cast iron and consequently should be as low as possible in castings where high induction and high permeability are desired. Also the remanent magnetism and coercive force decreases so that cast irons with manganese are not suitable materials for permanent magnets.

Manganese aids in counteracting the effect of phosphorus, which tends to produce large crystals, thus increasing the liability of the metal to check. By reducing the crystal size with manganese this checking tendency is decreased. More than 0.4 percent of manganese must be present in cast irons to cause any appreciable effect on mechanical properties. Increasing manganese results in some increase in tensile strength.

There is no influence on elongation by manganese up to 1 percent content (236), but higher percentages than 1 percent cause a decrease in elongation. By long annealing the manganese content may be somewhat higher than 1 percent without affecting the elongation adversely.

The retardation in cooling corresponding to the transformation of gamma into alpha iron sinks with increasing manganese content to lower temperatures with increasing manganese percentages until at about 8 percent manganese the thermal irregularities disappear entirely.

An expansion takes place corresponding to the gamma-alpha transformation which exerts an effect opposite to that of shrinkage. For this reason the low-manganese irons show a distinct expansion in the transformation region. At higher manganese percentages the transformations require longer periods and the temperatures at which they occur are lower.

Consequently, the manganese in cast irons must be definately controlled within certain percentages, depending on the grade or purpose for which it is used.

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